2.00 MATERIALS:-

The raw materials used are

a) Bauxite Residue: Red Mud
b) Magnesium Oxide
c) Lime grits (Calcium Oxide)
d) Barium Hydroxide
e) Sodium Carbonate
f) Sodium Hydroxide Pellets
g) Spent Liquor

2.01 a) Red Mud

The red mud was generated from alumina refinery plant of M/s National Aluminium Company Limited, Damanjodi & disposed it to Thick Thin Disposal of Red Mud Pond. Approximately 200 kg of red mud was collected from Red Mud Pond of NALCO Alumina Refinery Plant of Damanjodi. After proper coning & quartering red mud sample was grinded to ~53 Micron size in a Pulverizer.
2.02  b) Magnesium Oxide

Magnesium oxide (Light) Extra pure Grade supplied by Loba Chemie Pvt. Ltd., was used in sintered Mixture.

2.03 (c) Lime grists (Calcium Oxide)

Lime grists are supplied by Rajasthan & Katney & are used in causticization plant of Alumina Refinery Plant of Damanjodi. These lime grists are also used as Filter aid in Kelley filter of Alumina Refinery Plant of Damanjodi. The disposed lime grists was collected from lime handling plant & after proper coning & quartering it was grinded to 200 Micron size by a Pulverizer. These fine lime grists were used in Sintered Mixture.

2.04  d) Barium oxide

Barium oxide purified (LR) Grade supplied by S.D. fine-chem Ltd., Boisar was used in sintered Mixture.

2.05  e) Sodium Carbonate

Sodium Carbonate supplied by Qualigens fine-chem Ltd., Bombay was used in sintered Mixture.
2.06 f) Sodium Hydroxide Pellets

Sodium Hydroxide pellets supplied by Merck was used during leaching of red mud & sintered products.

2.07(g) Fresh Spent Liquor

Fresh Spent Liquor having Na$_2$O(C) of 145-175 gpl was collect from Alumina Refinery plant of M/s National Aluminium Company limited, Damanjodi. These different concentration of liquor are used for leaching of red mud and sintered products.

2.08 Preparation of 0.01 M Standard EDTA Solution

Approximately 3.7224 gms powered ethylenediaminetetraacetic acid sample was taken in a 500 ml beaker & about 200 ml de-mineralized water was added. The above solution was stirred in a magnetic stirrer so that ethylenediaminetetraacetic acid was completely dissolved. Then the above dissolved solution was transferred to a 1000 ml volumetric flask with the help of funnel. The beaker was rinse with 4-5 times de-mineralized water & transferred the water to the volumetric flask. Then de-mineralized water was added upto the mark with the help of wash bottle. The standard EDTA solution was used for the analysis of Alumina of filtrate of sintered products after leaching with caustic solution by titration method.
2.09 Preparation of Standard Zinc-Acetate Solution

Approximately 2.1949 gms of powdered Zincacetate sample was taken in a 500 ml beaker & about 200 ml de-mineralized water was added. The above solution was stirred in a magnetic stirrer so that Zincacetate was completely dissolved. Then the above dissolved solution was transferred to a 1000 ml volumetric flask with the help of a funnel. The beaker was rinse with 4-5 times de-mineralized water & transferred the water to the volumetric flask. Then de-mineralized water was added upto the mark with the help of wash bottle. The std Zincacetate solution was used for the analysis of Alumina of filtrate of sintered products after leaching with caustic solution by titration method.

2.10 Estimation of alumina of liquor by EDTA Titration Method

2.10.1. SCOPE

2.10.1.1 This standard covers the determination of alumina in bauxite.

2.10.2. SAMPLING

2.10.2.1 Sample shall be drawn and prepared as per the method prescribed in 2 of IS: 2000 ( Part 1 )-19857.

2.10.3. QUALITY OF REAGENT

2.10.3.1 Unless specified otherwise, analytical grade reagents and distilled water shall be employed in the test.

2.10.4. DETERMINATION OF ALUMINA

2.10.4.1 Complexometric Method
2.10.4.1.1 **Outline of the Method** - From an aliquot of the main solution, after dilution iron and titanium are precipitated by treatment with caustic soda solution. The precipitate is filtered through dry filter and alumina in the filtrate is determined complexometrically.

2.10.4.1.2 **Reagents**

2.10.4.1.2.1 **Caustic soda** - 20 percent (m/v).

2.10.4.1.2.2 **Concentrated hydrochloric acid** – specific gravity = 1.16 (conforming to IS : 265-1976).

2.10.4.1.2.3 **Sodium carbonate** - solid.

2.10.4.1.2.4 **EDTA (0.05 M)** - Dissolve about 18.64 g of the di-sodium salt of EDTA $\text{[CH}_2\text{N(CH}_2\text{COOH)}\text{CH}_2\text{COONa}]}_2\text{2H}_2\text{O}$ in water and transfer to a 1000-ml volumetric flask, dilute to the mark and mix.

2.10.4.1.2.5 **Methyl red indicator solution** – 0.1 percent (m/v) in rectified spirit.

2.10.4.1.2.6 **Dilute hydrochloric acid** - 1:1 (v/v).

2.10.4.1.2.7 **Buffer solution (pH 5.3)** - Dissolve 21.5 g of sodium acetate (CH$_3$COONa) in 300 ml water, add 2 ml glacial acetic acid and dilute to one litre.

2.10.4.1.2.8 **Standard zinc solution (0.05 M)** - Dissolve 3.26 g of electrolytic zinc granules (99.95 percent purity) in dilute hydrochloric acid(1:1) and evaporate the solution to 1 to 2 ml, dilute with water add 50 ml buffer solution (pH 5.3), mix, make up, the volume to one litre. Standardize against standard aluminium solution following the method for determination of aluminium.

2.10.4.1.2.9 **Standard aluminium solution (0.05 M)** - Weigh accurately 1.3490 gm of pure aluminium wire (99.9 percent) in a 500.ml beaker containing 50 ml of water and
50 ml concentrated hydrochloric acid. Heat the solution to dissolve the metal. Cool and dilute the solution to 1000 ml in a volumetric flask. ( 1 ml = 0.002550 g \( \text{Al}_2\text{O}_3 \) ).

2.10.4.1.2.10 *Xylenol orange solution* - 0.5 percent (m/v) in water acidified with 2 drops of dilute hydrochloric acid (40 percent).

2.10.4.1.2.11 Ammonium fluoride - solid.

2.10.4.1.3 *Procedure*

2.10.4.1.3.1 Pipette out 50 ml aliquot from the main solution [see 5.3.3 of IS : 2000 (Part 2) -1985 ] into 400-ml beaker and neutralize the solution with caustic soda solution. Dissolve the precipitate formed in minimum quantity of concentrated hydrochloric acid and pour the solution slowly with constant stirring to a 200 ml volumetric flask containing 25 ml of caustic soda solution and 1 g sodium carbonate. Keep this on the water-bath for about an hour and then cool to room temperature. Make up the volume to the mark with water and shake thoroughly. Filter dry and collect the filtrate in a dry beaker or dry polythene bottle.

2.10.4.1.3.2 Pipette out an aliquot (100 ml) from the filtrate to a 250-ml conical flask. Add about 30 ml of 0.05 M EDTA solution and a drop of methyl red indicator. Neutralize the solution with dilute hydrochloric acid, add 15 ml buffer solution and boil the solution for about 2 minutes. Cool to room temperature and titrate with standard zinc solution using 2 to 3 drops of xylenol orange indicator. The colour changes from yellow to red. Add about 2 g of ammonium fluoride to the solution and boil the solution for about 2 minutes. Add 10 ml buffer solution cool to the room temperature and then titrate with standard zinc solution adding a drop of xylenol orange indicator. The end point is from yellow to pinkish red. The percentage of alumina is calculated from the titrate value of second titration with zinc as given by equation (1).
2.10.4.1.4 Calculation

\[
\text{Alumina ( Al}_2\text{O}_3 \text{), percent } = \frac{(A \times B) \times 100}{C} \quad (1)
\]

where

\(A\) = ml of zinc solution required for second titration,

\(B\) = equivalent Al\(_2\)O\(_3\) (in g) per ml of zinc solution, and

\(C\) = mass in g of the sample as represented by the aliquot taken.

NOTE - This method is applicable when CaO and MgO is < P3 percent (m/m).

2.11 Heat Treatment Operation

Furnaces

Two furnaces were used for heat treatment

1. Muffle furnace where maximum temperature can be achieved up to 1200\(^\circ\)C as given in fig 1.

2. High temperature furnace where the maximum temperature can be maintained up to 1600\(^\circ\)C as given in fig 2 and 3.

2.11.1 Muffle Furnace

It was supplied by M/s Therek Furnaces, Bangalore. The size of the furnace was 15x15x30 cm. The total length of kanthal wire required was 200 cm. Kanthal wire of 2 mm diameter was wound over the muffle embedded with refractory cement. The muffle
was surrounded by fire clay insulating brick. Chromel-alumel thermocouple was used for measuring the temperature having a digital system. The desired temperature could be controlled by an electronic regulator with an accuracy of \( \pm 5 ^\circ C \).

### 2.11.2 High temperature furnace

The high temperature furnace was supplied by M/S Essco furnaces, Madras. The size of the furnace was as shown in fig. 2 & 3.

**Fig. 1 Muffle Furnace**
Fig. 2 High Temperature Furnace
Fig. 3 High Temperature Furnace
80x80x60 cm enclosed by an outer steel cabin. The heating chamber (36x18x12.5 cm) of the furnace was provided with 8 number of ‘U’ type molybdenum silicide heating electrodes. The electrodes were hung over high alumina heat resistant bricks. The heating electrodes provided by the furnace were 50 cm. in length. The upper parts of the electrodes having 1.2 cm. diameter were attached by flexible aluminium strips to copper strips. The copper strips were connected to a variable 3 phase step down transformer. The electrodes were heated at low voltage (8 to 15 V) and high current (300-500 amp.). The temperature of the furnace could be increased at the rate of 10 ⁰C/min. The heating zone of the furnace was insulted by heat resistant alumina bricks. A Pt/Pt-Rh (13%) thermocouple was used for measuring the temperature with digital display system. In normal operation the life of electrodes are 1000 hours. The longitudinal and cross sectional view of the furnace are shown in Figs. 1 and 2. Accuracy of temperature was ± 10°C.

2.11.3 Reactor

A specially designed reactor was used for heat treatment operation. The drawing of the high alumina brick reactor is shown in Fig. 3. The reactor was mechanised out of solid high alumina brick in NALCO workshop, Damanjodi.

This reactor was rectangular consisting of a lid and a rectangular hollow cavity. The lid was covered in the reactor and made airtight by pasting with cement. The length of the reactor was 10 cm and the dimension of the hole was 8x4x4 cm.
2.12 METHOD-I

Following method has been adopted for study.

Approximately 100 kg of red mud was collected from red mud pond of NALCO Refinery plant of DAMANJODI.

After proper coning and quartering the mud sample was grind to -53mesh size by pulverizer.

The mud sample was characterized by:

(i) Chemical composition of red mud was analysed by classical method, XRF and the trace elemental analysis was carried out by AAS

(ii) Mineralogy by XRD and the surface morphology study was carried out by Scanning Electron Microscope.

The Double Digestion study was carried out at (a)–various temperature, (b)–residence time, (c)–caustic concentration and (d)–Target RP

2.13 METHOD-II

Thermo-chemical sintering methodology has been adopted for study.

The mud sample was mixed with divalent alkaline earth metal oxides like CaO, MgO, BaO and Soda ash (Na₂CO₃) and sintered at different temperature as per experimental conditions in Table-2. Resultant sintered mass was grinded and leached at 105°C with 80 g/l of Sodium Hydroxide for 1 hour to optimise sintering temperature, time and quantity of additive for the extraction efficiency.
### Table-2

**Experimental conditions**

<table>
<thead>
<tr>
<th>Sl.No</th>
<th>Composition of Sinter Mixture. [Red Mud + Divalent alkaline earth metal oxide (i.e. CaO, MgO or BaO) + Na$_2$CO$_3$]</th>
<th>Sintering Temperature in °C</th>
<th>Retention time in Hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100 10 15 900 1 2 3 4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>100 10 20 900 1 2 3 4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>100 10 25 900 1 2 3 4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>100 15 10 1000 1 2 3 4</td>
<td></td>
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<tr>
<td>5</td>
<td>100 15 20 1000 1 2 3 4</td>
<td></td>
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</tr>
<tr>
<td>6</td>
<td>100 15 25 1000 1 2 3 4</td>
<td></td>
<td></td>
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<tr>
<td>7</td>
<td>100 20 10 1100 1 2 3 4</td>
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<tr>
<td>8</td>
<td>100 20 20 1100 1 2 3 4</td>
<td></td>
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</tr>
<tr>
<td>9</td>
<td>100 20 25 1100 1 2 3 4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.14 Laser Particle Size Analyzer

The coherent light from a helium–neon power laser passes through a liquid with a suspended powder sample causing diffraction of the beam. The energy distribution in the energy pattern observed which depends on the size of the diffracting elements. If all the elements are spherical and of the same diameter, the energy diffraction distribution follows the AIRY law, i.e. a series of concentric rings is formed, the diameters of which are related to grain size; the longer the grains, the closer the rings. On the other hand, if the particles are of different diameters, the diffraction pattern is more uniform.

The LASER granulometer used here is of M/S CILAS, France, Model-715 make.

The main component of model 715 granulometer are a) the Laser emitter, b) the suspension liquid circulation system, c) the detection system, d) the computer, e) the control panel, display and print out of results, f) the power supply.

The operating characteristic of this granulometer are:

<table>
<thead>
<tr>
<th>I) Measured particle diameter</th>
<th>0-192 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>II) Measured print out rate</td>
<td>one every 25 seconds.</td>
</tr>
<tr>
<td>III) Reference cells</td>
<td>Silicon photo detector.</td>
</tr>
<tr>
<td>IV) Photo detector</td>
<td>Silicon multi cell consisting of 15 measurement cells</td>
</tr>
</tbody>
</table>
Here the sample which is to be analysed vary from 0.1 to 1.0 gm in liquid suspension.

2.15 Optical Microscopy

The basic analytical procedure required for characterisation of the red mud is microscopy techniques are:

a. Optical Microscopy
b. Scanning Electron Microscopy (SEM) with EDAX attachment
c. Transmission Electron Microscopy (TEM) and
d. Scanning Transmission Electron Microscopy (STEM)

Optical microscopy being easily available, and as the sample preparation method does not require any complicated procedure, it has been found to be universally used. Optical microstructure [88] is delineated by observation and analysis systems that respond to reflection and refraction activity of carefully prepared micro sections. After the surface is properly polished and often impregnated with controlled surface treatment such as chemically acid ;basic etch ants ; oxidising etch ants ; or colouring effects produced by thermal oxidation or by adsorption staining etc.

The essential parts of an optical microscope are:

a) Condenser-filter system for light sources, b)Illuminator, c)Objective system, d) Occular system and e) Photographic system.

A metallo graphic microstructure using reflected beam is commonly used for studies of red mud as well as sintered red mud products, solid particles, platelets & even powered samples. Polarised beam and stereomicroscope with video arrangements are also often used for similar studies. A magnification up to 1000x can be expected in
optical microscope. A lietz Orthoplan microscope and Labolux optical microscopes have been used. Photomicrographs were taken by using blue filter. Red mud and sintered red mud were examined as such, where as the metal composite samples were mounted on thermo setting resins. The mounted samples were polished firstly with emery paper on an automatic polishing machine followed by fine polishing with magnesium oxide. The red mud and sintered red mud samples before and after leaching were etched with dilute HF; 2 drops of acid was added to the red mud and sintered red mud, washed and then dried before examination. The micrographs presented in the thesis have a magnification of 65X, and 180X, though the studies have been made up to 1000 X. Only the representative micrographs are shown here.

### 2.16 Scanning Electron Microscopy

SEM is a very useful in detecting & identifying presence of mineral phases in red mud as well as sintered products of red mud and leaching products of red mud. In case of red mud composites, the formation of phases like sodium aluminate, respective divalent alkaline earth metal silicate, divalent alkaline earth metal ferrites, divalent alkaline earth metal titanate, Sodalite, Cancrinite, Hematite, Goethite, Boehmite & Gibbsite can be identified by seeing the morphology of above phases at magnification of 2.00 KX to 5.00 KX. Only the representative micrographs are shown here.

The usual micrograph produced from the optical microscope or from the transmission electron microscope is a two dimensional image. The optical microscope presents an image in two dimensions because it has a very limited depth of field, which
means that it can be focused sharply in one plane only at low magnification (below roughly 200 diameters). The optical microscope is useful for showing the shape of the specimen in depth.

SEM is able to provide three-dimensional images because in normal mode of operation, it records not only the electrons passing through the specimen but also the secondary electrons that are released from the samples by electron beam imaging on it. The sample can be of any size and thickness that will fit in the instrument vacuum chamber. The secondary electrons do not have to be focused but are simply collected. Moreover, because of the envelope of impinging beam resembling to a sharp needle, the instrument achieves a great depth of field \[89\]. It has a long range of magnification, 30 diameter to about 3, 00, 000 diameters, the resolution being about 100°A.

SEM has four principal parts: a) an electron optical system that produces the scanning electron probe, b) a sample chamber where interaction between the probing electron beam and the material of the specimen produces the information signals c) a detection system that collects the information carrier emitted by the sample and amplifies the resulting electrical signals and finally, d) the display system that sequentially displays the information.

Micrographs can be taken with the help of a camera as well as Lexmark Laser printer attached to the instrument. Before analysing the specimen, it is required to make it conducting by coating a conducting layer of carbon, silver or gold or platinum, done by vacuum evaporation or ion sputtering technique. The conducting samples do not require any coating.
A commercial SEM has normally provisions for only the secondary electrons, but it has also provisions for auger electron, back scattered electrons, characteristic X-ray, cathodo luminiscence, photons and what is important is x-rays. Quantitative determination of most of the elements in periodic table [90] (from berillium to uranium) is also possible with X-ray spectrometer attached to SEM.

The SEM used here is of LEO, Electron Microscopy, Model 430, Make: United Kingdom England having wave length spectrometer. The samples have been coated with gold, and viewed in spots, areas, and as a whole.

2.17 X-Ray Fluorescence Spectrophotometry

EDXRF is an instrumental technique for non-destructive elemental analysis. The term XRF is generally applied when X-ray photons used to generate characteristic X-rays in the elements from the specimen. The most commonly used sources of such X-rays (in the 2-100 KeV range) are from radio isotope X-ray tubes. The classical XRF spectrometer which has been available, uses crystal structure to resolve the X-rays eliminating from X-ray fluorescence in the irradiating specimen.

The crystals diffract the characteristic X-rays from the elements in the specimen allowing them to be separated and measured. The characteristic fluorescent X-rays are said to have been separated from each other by the process of “wave length
dispersion” (WDXRF). Each element emits characteristic lines which can be separated by WDXRF before being individually counted. For each line and diffracting crystal, one can set a detector at a particular angle (from the Bragg’s equation) and collect the X-ray primarily from the element [91].

The WDXRF system uses the Si(Li) (Lithium drifted Silicon) detector to simultaneously collect all X-ray energies emitted from the specimen. Each detected X-ray photons give rise to a signal is proportional to the energy of the detected X-rays and when amplified and digitised can be passed to multi channel (MCA), which display a histogram of a number of X-rays (intensity) against energy. The incident photons, therefore, have been electronically separated according to their energy.

An EDAX instrument (Make: Philips, Model No. PW 2400) was used here, having Si (Li) detector at 160 ev. and 5.9 Kev.

### 2.18 X-Ray Diffractometry

X-Rays can be used for chemical analysis in several ways viz. emission, absorption and diffraction. The most widely used method of X-rays in analytical work is the diffraction of X-rays from the plane of a crystal. The X-ray diffractometry is based on Brag’s equation [92] which gives the condition of X-rays from the set of atomic planes. It states (equation 2)

\[ n\lambda = 2d \sin \theta \] (2)
Where \( n \) is the order of reflection, \( \lambda \) is the wavelength of characteristic X-ray beam, \( d \) is the inter planar spacing in the crystal lattice and \( \theta \) is the angle of diffraction.

Thus for a given set of lattice planes in a fixed value, if homogeneous X-rays of definite wave length are used, the possibility of getting maximum reflection depends on \( \theta \), where \( \theta \) is the angle which the X-rays make with the plane of a crystal. If \( \theta \) is regularly increased, a number of positions corresponding to \( n = 1, 2, 3, \ldots, n \), will be found at which the reflections will be maximum. The instrument used is of Rigaku, Japan (Model: Dmax 2200) records the 2\( \theta \) values along with the intensity for the samples directly. The sample is powered in an agate mortar and pestle and then sprayed over the sample slot (36 mm \( \Phi \) x 1.0 mm t). The 2\( \theta \) values recorded were normally from 5\( ^\circ \) to 70\( ^\circ \). The voltage of the generator was kept at 40 KV and the current at 30 ampere with a copper target (K\( \alpha = 1.54186 \) \( \AA \) with Nickel Filter). The speed of the goniometer was maintained at 0.5\( ^\circ \)/minutes. Only the representative XRD scan of red mud, sintered red mud and leached red mud are shown here.

### 2.19 TG/DTA Analyzer

Thermal analysis constitutes “a group of techniques in which a physical property of a substance of its reaction products is determined as a function of temperature, while the substance is subjected to a controlled temperature programme”[93].
The most widely used techniques are TG (Thermogravimetry) and DTA (Differential Thermal Analysis).

In thermogravimetry (TG), the change in sample mass (mass loss or gain) is determined as a function of temperature or time.

Differential thermal analysis (DTA) is a thermal technique in which the temperature of a sample compared with the temperature of a thermally inert material is recorded as a function of temperature as the sample is heated or cooled at uniform rate.

Temperature changes in the sample are due to endothermic or exothermic enthalpy transition or reactions such as those caused by phase changes, fusion, crystalline structure inversion, dehydration reaction, dissociation or decomposition reaction, destruction of chemical lattice structure, and other chemical reactions. The temperature changes occurring during these chemical or physical changes are detected by a differential method.

For thermal analysis, the sample and reference material are usually taken in a small crucible made of Rh-Pt, Ta, Quartz or Alumina. A programmable furnace provided with arrangements for cooling by water circulation is used for heating the sample and reference material. Experiments under controlled atmospheres are also possible as the furnace can be purged with the desired gas at a constant rate. Calcined alumina is usually taken as the reference material. Calibration of instrument is carried out using standard materials such as copper sulphate, calcium oxalate.

Thermograms of the materials under study were taken in a Seikho Japan Make (Make Exstar-6300) simultaneous thermal analyzer.
The Exstar 6300 Model simultaneous thermal analyzer is designed to give simultaneous records (i.e., weight Vs. time or temperature) and differential thermal analysis curves (i.e., $\Delta T$-t, where $T$ is the temperature difference between the sample and reference material), which simultaneously eliminates the problems of correlating TG and DTA data for the same substance.

2.20 **Sanda Thermometric Titrometry**

Thermometric titrimetry has a long association with the production of alumina from bauxite & bauxite residue; where it has traditionally been applied to the determination of caustic and aluminate contents of recirculating “Bayer Process” liquors\(^{[94]}\). However, the versatile nature of this technique means that it can be applied to other important areas of process and quality control in alumina refining.

2.21 **INTRODUCTION**

In the thermometric titrimetry, titrant is delivered at a constant rate, and the rate of heat evolution or absorption is substantially constant while unreacted analyte remains in the sample solution. When all analyte is consumed, the temperature rate increase or decrease is important, it is unnecessary to calibrate the sensing thermistor (although this can be done if desired). It is also unnecessary to use hermetically sealed calorimeter vessels; Styrofoam coffee cups make ideal titration vessels in most aqueous titrations. Otherwise, polypropylene beakers or small “thermos” flasks may be used.
Thermo titration is an ideal technique for process and quality control in industry as previously stated, the sensing thermistor does not require calibration, and will last indefinitely (provided that the protecting glass envelope is not broken or chemical attacked). The same sensor may be used for acid-base, redox, and complex metric titrations, as well as those where precipitates are formed. In many cases, it is unnecessary to dilute the sample solution prior to analysis. Non-aqueous titrations may be easily performed. Applications so far developed span many industries; including mining, hydrometallurgical, metal finishing, catalysts, pigments and fillers, petrochemicals and food.

Although thermo titrimetry can trace its origins back to the early years of the century, it is not only since the advent of fast response thermistors in the 1950’s that the technique has become of practical use to analysts. The first really practical exponent of this technology was aluminium major Alcan limited, who had developed it for the analysis of Bayer Process liquors. The electronic basis of the thermo titrator has been traditionally a Wheatstone bridge, of which the thermistor forms one arm, although other variants are possible. The thermo titrator consists of three modules:

-A stepper-motor driven precision burette pump

-A control module which controls input and output signals

-A personal computer.
2.23 Procedure for Analysis of Sodium Aluminate (Bayer Process) Liquors.

An aliquot of Bayer Process of sodium aluminate liquor is treated with a solution of an aluminium complexing ion, preferably tartarate. In complexing aluminate species in solution, one gram ion of hydroxyl is released for each gram atom of aluminium in solution:

\[
\text{Al(OH)}_4^{-} + n(\text{Tart})^{2-} \xrightarrow{\text{< - >}} \text{Al(OH)}_3(\text{Tart})n^{2-} + \text{OH}^{-} \quad (3)
\]

Together with “free” hydroxyl ions already present in solution, these hydroxyls are titrated with protons (acid), to thermometrically determined end point.

\[
\text{H}^{+} + \text{OH}^{-} \xrightarrow{\text{< - >}} \text{H}_2\text{O} \quad \text{H} = \Delta -56.2 \text{ KJ/Mole} \quad (4)
\]

The reaction:

\[
\text{H} + + \text{CO}_3^{2-} \xrightarrow{\text{< - >}} \text{HCO}_3^{-} \quad \Delta \text{H} = -14.8 \text{ KJ/Mole} \quad (5)
\]

Does not interfere, due to the large differences in reaction enthalpies.

After the caustic titration is complete, fluoride ion is added to break the aluminate complex, releasing 3 gram ion hydroxyl for every gram atom aluminium present.

\[
\text{Al(OH)}_3(\text{Tart})n^{2-} + 6\text{KF}^{-} \xrightarrow{\text{< - >}} K_3\text{AlF}_6 + n(\text{Tart})^{2-} + 3 \text{OH}^{-} \quad (6)
\]
These hydroxyls are then titrated with hydrogen ions to the same thermometrically-determined end point. Reference may also be made to Van Dalen & Ward’s original paper on this method.

It is convenient to determine carbonate sequentially after the caustic and alumina determinations. The thermo titrator is sufficiently sensitive to determine the carbonate end point, in spite of the relatively low reaction enthalpies. The protonation of bicarbonate may also be observed:

\[
\text{HCO}_3^- + \text{H}^+ \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{H}_2\text{O} + \text{CO}_2,
\]

\[\Delta H = -7.66\text{KJ/Mol.}\] (7)

However, the reproducibility afforded by this reaction is not as good as for reaction (3), and is not used for the determination of the carbonate content of the liquor.

2.21 Atomic Absorption Spectrophotometry

AAS has been the most effective of all the instrumental techniques for quantitative determination of trace elements in parts per million (ppm). This method provides measurement of total metal ion content in the sample independent of molecular form in which the metal ion may exist in liquid.

It is based on the measurement of intensity of radiation emitted when the atoms and molecules of a sample raised to an excited state in the flame, returns to a lower ground state. Excited species emit radiations that are characteristic for each element.
The excited atoms which are unstable and when they return to a lower energy state, they emit luminous radiations. If $E_2$ and $E_1$ represents the higher and lower energy levels respectively, the frequency of radiation emitted during the quantum jump may be expressed by Bohr’s equation (8).

$$E = E_2 - E_1 = h\nu = hc/\lambda \quad (8)$$

Where ‘c’ is the velocity of light, ‘h’ is the Plank’s constant, ‘$\nu$’ is the frequency of emitted light and ‘$\lambda$’ is the wave length of radiation absorbed [95]. The wavelength emitted gives an indication of the element present in the sample while the intensity of the radiation helps in their quantification.

The essential parts of AAS are: a) nebulizer, b) burner, c) hollow cathode lamp, d) monochromator, e) photomultiplier, f) amplifier and g) processor.

The experimental conditions of different elements are as follows:

<table>
<thead>
<tr>
<th>Elements</th>
<th>Lamp Current (ma)</th>
<th>Slit Width (nm)</th>
<th>Wave Length (nm)</th>
<th>Flame</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>4.0</td>
<td>0.5</td>
<td>422.7</td>
<td>N₂O/C₂H₂</td>
</tr>
<tr>
<td>Mg</td>
<td>4.0</td>
<td>0.5</td>
<td>285.2</td>
<td>N₂O/C₂H₂</td>
</tr>
<tr>
<td>V</td>
<td>20.0</td>
<td>1.0</td>
<td>318.5</td>
<td>N₂O/C₂H₂</td>
</tr>
<tr>
<td>Mn</td>
<td>5.0</td>
<td>0.2</td>
<td>279.5</td>
<td>AIR/C₂H₂</td>
</tr>
<tr>
<td>Na</td>
<td>5.0</td>
<td>1.0</td>
<td>589.0</td>
<td>AIR/C₂H₂</td>
</tr>
<tr>
<td>K</td>
<td>5.0</td>
<td>1.0</td>
<td>766.5</td>
<td>AIR/C₂H₂</td>
</tr>
</tbody>
</table>
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N\textsubscript{2}O and C\textsubscript{2}H\textsubscript{2} used are of IOLAR grade from Indian Oxygen Co., Visakhapatnam. The AAS here is of M/S VARIAN , Make Australia,model-1475. It has a micro processor system and the command can be through a HP-85 computer. The analysis data are printed with deduction of back ground correction which had been programmed.

**Analysis of Na,K and Mn**

0.25 gms of sample was taken in a previously cleansed, dried and then weighted APR crucible (Gold-Platinum –Rhodium). The composition of crucible is as follows: Gold~3%, Platinum~87 %, Rhodium~10 %. The above alloy is preferred to platinum crucible because of the corrosion problem in case of the later.

2.4 gm of anhydrous lithium tetraborate (Li\textsubscript{2}B\textsubscript{4}O\textsubscript{7}) of GR grade was added to the sample in the crucible. The mixture was thoroughly homogenized with a Pt rod before it was kept in a muffle furnace. The temperature of the furnace was slowly increased to 1000 °C and was maintained for 30 minutes. The crucible with fused mass was carefully taken out of the furnace with the help of a platinum tip tongue and cooled on a platinum plate. When it was thoroughly cooled, it was transferred to a beaker containing hot (80 °C) HCl of 10 % concentration. The solution was then stirred over a hot plate having a magnetic stirrer at controlled speed (at 90 °C) till the fused mass got completely dissolved in the acid solution which took about one hour. It is to be seen that no fused mass sticks to the crucible. The solution was then
transferred to a 250 ml volumetric flask and the volume was made with redistilled water.

**Analysis of Ca, Mg and V**

0.25 mg of substance was taken in a Pt crucible which was thoroughly cleaned and dried before hand. Then 1.4 gms H\textsubscript{3}BO\textsubscript{3} and 2.5 gms Li\textsubscript{2}CO\textsubscript{3} was added to the platinum crucible. After homogenisation, it was kept in the furnace. The temperature was slowly raised from room temperature to 300\textdegreeC for 30 minutes and then again for 30 minutes at 1000\textdegreeC. The Pt crucible was taken out carefully from the furnace and cooled over a Pt plate. Then it was transferred into a beaker containing 150 ml of 10 \% HCl at 80\textdegreeC. The beaker along with the fused mass takes about 3 hours to get dissolved in acid solution.

The solution was transferred into a 250 ml volumetric flask and the volume was made with redistilled water.

**Analysis of Na\textsubscript{2}O**

GR grade NaCl (Emerck) was dried in an oven for 2 hours at 105\textdegreeC. Then it was cooled in a desiccator. 1.89 gm of NaCl was weighted into a cleaned dry aluminium foil and transferred into a one litre volumetric flask. Then the flask was filled with redistilled water and shaken thoroughly. 25 ml of aliquot was diluted to 100 ml (1 m=0.25 mgs of Na\textsubscript{2}O). A series of standard solution were made by adding 1, 2 or 3 ml of diluted solution from a micro burette into 250 ml volumetric flask
which contains 25 ml of the fused sample solution. Then the volumetric flask was diluted up to mark with redistilled water.

A blank solution was made by dissolving \( \text{Li}_2\text{B}_4\text{O}_7 \) in a beaker with 100 ml of 10 \% HCl and diluted up to 250 ml in a volumetric flask.

**Analysis of CaO**

1.785 gms of GR grade \( \text{CaCO}_3 \) (E Merck) was weighed and transferred to a one litre beaker, 200 ml of redistilled water was added to the beaker. 10 ml of HCl was added drop by drop to the beaker. After completion of the addition, the beaker was heated to boiling for 5 minutes. After cooling, the solution was transferred into one litre volumetric flask and diluted up to mark. 25 ml of the aliquot was diluted to 100 ml (1 ml =0.25 mg of CaO). A series of standard solutions were prepared by adding 1, 2 or 3 ml of diluted CaO solution to volumetric flask containing 25 ml of the sample solution. 10 ml of 10 gm/litre \( \text{La(NO}_3)_3 \) solution was added to the standard solution for avoiding the interference effects.

**Analysis of Mg**

4.19 gm of \( \text{MgCl}_2\cdot6\text{H}_2\text{O} \) was weighed into a 500 ml volumetric flask and diluted with redistilled water to get 1 mg of Mg. Standard solutions were made similar to the procedure for preparation of CaO standard solutions.
Analysis of K

1.907 gm. of dried KCl was dissolved in redistilled water and diluted to one litre, then 25 ml of aliquot was again diluted to 100 ml (1 ml = 0.25 mg of K). Standard solutions were prepared by adding 1, 2 or 3 ml of the diluted solution to the 25 ml of fused solution in a 250 ml volumetric flask. A blank solution was made by taking lithium tetraborate solution without sample.

Mn

4.5845 gm of MnCl₂.7H₂O was (E Merck) dissolved in one litre of water (1 ml = 1 mg of Mn).

V

1.0 gm of V₂O₅ GR of E Merck was dissolved in 10 ml of HCl and was diluted to get 1 mg of V₂O₅/ml, 10 ml of 10 g/l NH₄F was added to suppress the interference.

Method of Analysis

The concentration of the standards were kept in the inbuilt microprocessor of AAS. Normally three values were fed (for Na 0.5, 1.0 and 1.5 ppm in the present case). Then the standard solutions were aspirated and concentrations were checked.
The zero value was calibrated with blank solution. The concentration of the unknown solution was then read.

The concentration can be known either in absorbance or concentration mode. Before starting the calibrations the alignment of the monochromator light, by adjustment of the nebulizer, hollow cathode lamp and height of burner was thoroughly checked.