CHAPTER - 2

EXPERIMENTAL TECHNIQUES

2.0 Sample Preparation:

The samples used in these investigations were lignites from Neyveli Mine I and Mine II, Kutch (Panandharo) lignite and South Gujarat (Rajpardi) lignite. One bituminous coal sample from Singareni mine was also used. The samples, approximately 50 kg from each mine were purged with a mixture of nitrogen and carbon dioxide gas (98% N$_2$ - 2% CO$_2$) to drive out the entrapped air containing oxygen, sealed in polythene coated gunny bags and transported from mine site to the laboratory. The samples brought from the mine site were mostly of size 15mm and below. In the laboratory, the samples were initially crushed after partial drying in the atmosphere using rotary drum crusher to less than 5mm and stored in polythene bags after purging with nitrogen gas. Representative samples were then drawn from the above, whenever required, by quartering and coning. Grinding the above sample to get the required size was achieved using "RETSCH" Ultra Centrifugal Mill ZM1. During the sample preparation operations, dry ice was added to the sample to minimize oxidation. The substance to be ground was fed through the inlet hopper of the Ultra Centrifugal Mill, into the grinding chamber where it was picked up by the high
speed rotor and reduced in a fraction of a second between the rotor and the ring sieve. When the ground substance had reached the necessary fineness, centrifugal force expressed it through the ring sieve into the collecting pan. The sample from one mine was ground in bulk and used for all hydrothermal treatment studies so that the size distribution will be more or less the same for all experiments.

2.1 Proximate Analysis

Proximate analysis of the raw and the treated lignite samples consists of the determination of inherent moisture, volatile matter, ash and fixed carbon (by difference). A representative sample was ground to pass through 72-BS mesh and equilibrated at 60% humidity in a humidity chamber for 48 h. This sample was further used for both proximate and ultimate analyses. Proximate analysis was done using MAC-500 Proximate Analyzer, (LECO make). The above instrumental proximate analysis has been included as a standard method as per ASTM D5142-90. The microprocessor controlled instrument can perform multiple sample proximate analysis with a fully automated system. The microprocessor controls most of the functions and performs all the calculations in the analysis. The unit has a single furnace with a turn-table for the sample crucibles and an internal balance for weighing the samples during the analysis. Samples were
loaded into the tared crucibles, and the moisture was
determined by heating the samples in nitrogen atmosphere at
100° until a constant weight was obtained. The complete set
of crucibles was weighed every 3 min by the internal
balance. After the moisture determination, lids were placed
on the silica crucibles and the temperature of the furnace
was raised to 900° at a rate of 60° per min. The samples
were held at this temperature for 7 min and then weighed.
The volatile matter is the mass lost during this heating
step. The temperature of the furnace was dropped to 600°,
the lids were removed from the crucibles, and the samples
were ashed by raising the temperature of the furnace to 800°
and heating the samples in oxygen until a constant weight
was obtained. The fixed carbon by difference was calculated
by the instrument software and printouts were obtained.

2.2 Ultimate Analysis

2.2.1 Determination of Carbon, Hydrogen and Nitrogen

The determination of carbon, hydrogen and nitrogen were
carried out simultaneously using CHN-600 ELEMENTAL ANALYZER,
LECO Make. An ASTM Task group had made a draft proposal for
possible inclusion as standard method for the instrumental
determination of carbon, hydrogen, and nitrogen in coal.
An outline of the equipment is shown in Fig. 2.1. A weighed quantity of sample was burnt in pure oxygen at 950°. Carbon dioxide, water vapour, oxides of nitrogen, elemental nitrogen and oxides of sulphur were possible products of combustion. Oxides of sulphur were removed with calcium oxide in the secondary combustion zone so that water vapour can not combine to form sulphuric acid. The remaining gases of combustion were collected in a ballast volume and were allowed to mix thoroughly. For the nitrogen determination, a 10 ml aliquot was taken. The aliquot was carried by helium into a reagent train consisting of hot copper and a catalyst for the removal of O2 and the reduction of NOx to N2, sodium hydroxide for the removal of CO2, and magnesium perchlorate for the removal of H2O. The remaining elemental nitrogen was measured by the thermal conductivity cell. Simultaneous to the nitrogen measurement, the carbon and hydrogen infrared cells measure CO2 and H2O levels. The infrared cell outputs were linearized. (The thermal conductivity cell was already linear) and all outputs were multiplied by the appropriate calibration factor and "K-factor", the composite correction factor for barometric pressure, ballast volume, pressure and chemical interferences. Next, adjustments were made for blank and weight compensation. When these calculations were complete, the results for the three elements were displayed
Fig. 2.1 Simplified flow schematic of carbon, hydrogen and nitrogen determinator. (Leco make)
in weight percent. Using moisture content of the lignite samples the results were also calculated on a dry basis.

2.2.2 Determination of Total Sulphur

The total sulphur in the raw lignite and hydrothermally treated lignite samples were determined as per "ASTM D3177 - Total Sulphur Analysis in the sample of Coal and Coke, Method A- Eschka Method". The coal sample was ignited in intimate contact with Eschka mixture (2 parts by weight of magnesium oxide + 1 part by weight of sodium carbonate), the soluble sulphur compounds leached out and oxidized with bromine to form sulphates followed by acidification and precipitation as barium sulphate, which was filtered, ignited and weighed.

2.2.3 Determination of Oxygen

The percentage of oxygen was calculated as per ASTM procedure, by subtracting from 100 the sum of the other components of ultimate analysis viz carbon, hydrogen, nitrogen, sulphur, ash and moisture.

2.3 Determination of Equilibrium Moisture

The equilibrium moistures for lignites were determined according to ASTM-D1412 procedure. Equilibrium moisture or the moisture holding capacity is generally recognized as the
moisture content of the lignite/coal in equilibrium with a relative humidity of 96-97% at 30°. The hydrothermally treated lignite samples and demineralized water washed lignite samples were wetted to saturation. The samples were then dewatered under suction, care being taken not to dry the sample excessively. 5 g portions of the above samples were transferred to weighing bottles. The weighing bottles were then placed in a vacuum desiccator containing saturated solution of potassium sulphate. An excess of potassium sulphate must extend above the solution. The desiccator was then evacuated to a pressure of about 30 mm of mercury and placed in a constant temperature water bath regulated to 30° for 72 h.

After the equilibration period, the samples in the desiccator were returned to atmospheric pressure, removed, and weighed, followed by drying in a pure nitrogen atmosphere at 105° to constant weight. The equilibrium moisture was calculated from the loss in weight of the equilibrated sample.

For raw lignites alone, the samples were not saturated with demineralized water since loss of soluble inorganics such as alkali chlorides and sulphates will result in lower equilibrium moisture values.
2.4 Determination of Gross Calorific Value

Throughout these studies, the gross calorific value was determined using PARR ADIABATIC BOMB CALORIMETER and PARR 1720 CALORIMETER CONTROLLER.

The procedure for using the above equipment is specified in ASTM method D 2015-85. A weighed sample was burnt in an oxygen bomb covered with water in a container surrounded by a jacket. The jacket temperature was adjusted during the burning so that it was essentially the same as the calorimeter water temperature. The accurate temperature rise times the energy equivalent of the calorimeter gives the total amount of heat produced during the burning of the sample. The energy equivalent of the calorimeter was determined by burning standard samples of benzoic acid. After burning, the contents of the bomb were washed into a beaker and titrated with standard sodium carbonate solution to determine the amount of acid (HNO₃ and H₂SO₄) produced in the combustion. Correction for the amount of acid, the amount of fuse wire used in firing and the sulphur content were then made to the total heat produced in the calorimeter to determine the gross calorific value of lignite samples. The 1720 microprocessor based controller was used to
2.5 Determination of Forms of Sulphur

Since the hydrothermal treatment of lignite samples results in a cleaner fuel, the determination of the forms of sulphur viz pyritic sulphur, sulphate sulphur and organic sulphur in both raw and treated lignite samples is obviously important. The extent of removal of organic and pyritic sulphur after hydrothermal treatment needs to be estimated. The procedures for determining the forms of sulphur are described in ASTM method D 2492. In this method, the sulphate and pyritic sulphur were determined directly, and the organic sulphur was taken as the difference between the
total sulphur and the sum of the sulphate and pyritic sulphur.

2-5 g of the analysis sample was mixed with dil. HCl (2 volumes of HCl+3 volumes of water), and the mixture was gently boiled for 30 min. After filtering and washing, the undissolved coal was retained for the determination of pyritic sulphur. Saturated bromine water was added to the filtrate to oxidise the sulphur to sulphate ions and iron(II) to iron(III) ions. After boiling to remove excess bromine, the iron was precipitated with excess ammonia and filtered. The precipitate was retained for the determination of non-pyritic iron. The sulphate was then precipitated with BaCl₂, and BaSO₄ was determined gravimetrically, and sulphate-sulphur percentage calculated. The coal residue from the above sulphate estimation was treated with dil. HNO₃ and boiled for 30 min to oxidise iron (II) species to iron (III) and inorganic sulphur compounds to sulphate. The mixture was filtered, and iron in the filtrate determined by precipitation, dissolving in HCl and subsequent titration after reduction with SnCl₂ with K₂Cr₂O₇ after removing the colouration in the filtrate by the treatement with 30% H₂O₂.

% Pyritic sulphur = % pyritic iron x 2 x 32.06/55.85

where 2 x 32.6/55.85 is the ratio of sulphur to iron in
pyrite.
Organic sulphur = Total Sulphur - (Pyritic sulphur + Sulphate sulphur)

2.6 Determination of Carboxylic Acid Content in Lignites

Determination of carboxylic acid content was done as per the procedure originally developed by Schafer and other researchers. The lignite sample was demineralized as follows: 5 g of lignite of size - 44 μm was treated with 50ml of concentrated hydrochloric acid for 1h at 50°, filtered and washed. The residue was subsequently treated with 50ml of hydrofluoric acid under the same conditions. Finally, treatment with hydrochloric acid was repeated. The residue was washed with deionized water until no silver chloride formed upon addition of silver nitrate solution to the filtrate. 1 g of the above demineralized lignite was refluxed in an atmosphere of nitrogen with 100 ml of 0.5 M barium acetate for 20 h. The acetic acid liberated was titrated with 0.025 M barium hydroxide to pH 8.25 using phenolphthalein indicator. The result is expressed as milli equivalent of - COOH per g of lignite.
2.7 Determination of Composition of Coal Ash

Ash analysis of lignite samples before and after hydrothermal treatment is aimed at finding the changes in quantities of inorganic constituents during the treatment. The procedure for ash analysis is specified in ASTM method D2795 "Analysis of Coal and Coke Ash". Although the constituents are reported as oxides, they occur in lignite ash primarily as a mixture of silicates, oxides and sulphates. The silicates originate in the shale and clay minerals. The principal source of iron oxide is pyrite, which burns to form ferric oxide and sulphur oxides. Calcium and magnesium oxides result from decomposition of carbonate minerals, while the sulphates are formed from interaction between carbonates, pyrite, and oxygen.

During the preparation of the ash samples for analysis from lignite samples, care was taken to slowly burn the lignite to prevent the retention of sulphur as sulphate in the ash. If the rate of burning is too rapid, some of the sulphur oxides produced from burning pyrite may react with metal oxides to form stable sulphates. The result is that indefinite amounts of sulphur are retained which introduces errors into all the analytical results. 3-5 g sample of ash was prepared by placing the lignite sample (ground to pass
BS 72 mesh sieve) in a muffle furnace and gradually heating it so that the temperature reaches 500° in 1 h and 750° in 2 h. The mixture was then ground (to pass a BS 100 mesh sieve) and reignited at 750° for 1 h. The analysis of coal ash by ASTM method D 2795 involves a combination of methods to determine the amounts of SiO₂, Al₂O₃, Fe₂O₃, TiO₂, CaO, MgO, Na₂O, K₂O and sulphate as SO₃. Two solutions were prepared from the ash. Solution A was obtained by fusing the ash with Na₂CO₃ followed by dissolution of the melt in dilute HCl. This solution was used for the analysis of SiO₂, Al₂O₃, Fe₂O₃, TiO₂, CaO, MgO and sulphates.

Solution B was prepared by digesting the ash with HF first and then with HCl. This solution was used for the determination of Na₂O & K₂O. Spectrophotometric procedures were used for the determination of SiO₂, Al₂O₃ and TiO₂. A complexometric titration with EDTA was used to determine CaO and MgO while Na₂O and K₂O were determined by flame photometry.

2.8 Determination of Tar Content – Gray King Assay

An improved apparatus consisting of a furnace and a tubular retort made of quartz 30 cm long and 2 cm dia with one end closed was used to determine the tar yield of different lignite samples. The procedure is specified in International
Standard ISO 647 - "Brown Coals and Lignites - Determination of Yields of Tar, Water-Gas, and Coke Residue by Low Temperature Distillation - 1974-11-01". The open end of the tube was connected to a detachable quartz collecting vessel which was cooled by an ice bath. The gas yield could be measured using a gas burette. The furnace was heated to a temperature of 325°. 20 g of the dry sample ground to pass a 72-mesh BS sieve were then placed in the tubular retort and then flushed in a current of N2. The N2 flow was stopped. The open end of the retort was connected to the tar collection vessel and then to a gas burette.

The resistance of the furnace was adjusted so that the temperature reached 600° in 1 h. The furnace was maintained at 600° for further 15 min. The tar collected was weighed along with the vessel. The gas volume was measured in the gas burette and the weight of the coke formed was found out after cooling.

2.9 Thermogravimetric Analysis

Before treating the lignites hydrothermally and then testing the slurriability of the treated lignite samples, there is a need to assess the behaviour of the raw sample with respect to the release of volatiles with temperature, in nitrogen atmosphere.
The derivative thermogravimetric (DTG) output from a thermobalance system is plotted against temperature as the sample of lignite is heated at a constant rate in a flowing 99.99% pure nitrogen gas.

The apparatus used was the METTLER TA 3000 SYSTEM which consisted of a THERMO BALANCE (TG 50), a TA PROCESSOR (TC 10) and a matrix printer.

The dynamic mode of the test-run, the size of the TG.plot required, rate of increase of temperature of the furnace, the initial and final temperature, the type of evaluation required etc could be controlled by the TA 10 microprocessor.

The TG weighing system has a measuring range of 0 to 150 mg with a readability of one microgram. A platinum sample carrier, connected by a gold plated sling is hung from the microbalance into the tubular furnace. The micro balance rests over a platform beneath which a tubular furnace is mounted. The furnace can be lowered or raised to facilitate the loading of the sample into the furnace. The furnace has been provided with purge gas ON/OFF solenoid valves through a gas flow meter. Purge gas is admitted to the furnace from the top and exits at the bottom so that buoyancy created in the reaction zone due to gas evolution is reduced. The
maximum working temperature of the furnace is 1000°, with variable heating rates ranging from 1 to 100°/min.

Initially the TG furnace was lowered, a dried alumina crucible (150 µl capacity) was placed on the sample carrier, the furnace closed and locked. Purge gas (99.99% pure nitrogen gas) was admitted with a flow rate of 20 ml/min. at a pressure of 0.5 bar to ensure uniform flow. The balance tared, crucible loaded with 8.0 to 8.5 mg of lignite sample of the same particle size with which it was used in the hydrothermal treatment (80% through 75 microns). The sample weight was then determined.

The following parameters were furnished to the TA processor. These parameters were kept the same for all the samples tested so that the results can be compared very reliably.

Start temperature °C 40
Heating rate °C/min 30
End temperature °C 900
Time ISO min 0
Plot cm 15
Range FS mg 10
Offset % 90
Valve T/t 1/2 1
Fig. 2.2 Optical diagram of Malvern Particle Size Analyzer.

Fig. 2.2.1 Photograph of Malvern Particle Size Analyzer-2600 Series System.
The purge gas flow, the weight of the sample taken, and even the crucible were maintained the same for all the samples tested to get comparable results.

The in-built software helps to obtain the outputs of thermograms with reduced noise levels.

2.10 Particle Size Analysis

The particle size distribution of the lignite samples before and after hydrothermal treatment were analysed using MALVERN PARTICLE SIZE ANALYZER - 2600 SERIES SYSTEM.

The raw lignites and the hydrothermally treated lignites were introduced into the sample cell of the particle analyser in the form of dilute suspension in water.

The general pattern of the laser diffraction experiment is shown in Fig:2.2 and the Photograph is shown in Fig.2.2.1.

The light from a low power Helium - Neon laser, typically 18 mm dia was used as the analyzer beam. The particles were introduced to the analyzer beam by a sample cell. The light scattered by the particles and the unscattered remainder were incident on to a receiver lens. This receiver lens operates as a Fourier Transform lens forming the far-field diffraction pattern of the scattered light at its focal plane. Here a custom designed detector, in the form of a
series of 31 concentric annular sectors gathers the scattered light over a range of solid angles of scatter. Larger particles scatter the laser beam at low angles and small particles scatter at high angles. When a particle scatters light it produces a unique light intensity characteristic with angle of observation. A particle scatters light so that the measured energy on the detector has a peak at a favoured scattering angle which is related to its diameter.

Large particles have peak energies in small angles of scatter and vice versa. A computer predicts the scattering signal that would be received from a wide range of materials at a given size. Thus, a table will be obtained which characterizes how a unit volume of material of a range of sizes throughout the working range scatters light. The computer then deduces the volume size distribution that gives rise to the observed scattering characteristics. The computer achieves this by a process of constrained least squares fitting of the theoretical scattering characteristics to the observed data.

In all the measurements made, the Rosin-Rammler distribution was assumed and the best fit of the assumed functional form of distribution to the observed data was obtained using the
computer. Uniquely a 300 mm lens was used which will measure a range of particle sizes between 5.8 μm to 564 μm.

2.11 Determination of Surface Area

Surface area for Neyveli raw and hydrothermally treated lignite samples were determined with the idea to study the variations of surface area with hydrothermal treatment temperatures, and corresponding pressures.

It is reported that the standard BET method for surface area measurement using nitrogen adsorption at -196° gives unrealistically low surface areas for most coals, and particularly for low rank coals. Australian and German soft brown coals have nitrogen BET areas in the range 1-5 m²/g, two orders of magnitude lower than those obtained by the other methods like the ones which use CO₂ adsorption at 25° and water adsorption at ambient temperature. These values are low because the micropore structure of such coals is so fine that it is virtually inaccessible to nitrogen at -196°, since the penetration of the pore structure is by an activated diffusion process.

It is reported by Allardice that the surface area of brown coals can be estimated by the BET method at ambient temperatures by using water adsorption isotherms, and assuming a cross sectional area for the water molecules the same as that in normal liquid packing. For Australian brown coals, this method yields areas greater than 200 m²/g. For
low rank coals most of the surface is covered with hydrophilic oxygen containing functional groups. The estimates of surface area obtained by water adsorption though appear to be realistic, it is doubtfully exaggerative since multilayers may be formed over water molecules of the monolayer fixed to the coal surface by hydrogen bonding. But the BET theory assumes a monolayer formation only.

Nitrogen adsorption method was used in all the investigations to determine the surface area corresponding to macro-pores of raw and hydrothermally treated lignites. The equipment used was QUANTASORB - SURFACE AREA ANALYZER. Initially the sample was degassed at 105° in a current of helium for three hours. The flow control accessory was adjusted to get a supply of carrier gas and adsorbate gas mixture with the required relative pressure of adsorbate. The sample was subjected to nitrogen gas adsorption, followed by desorption when the Dewar flask containing liquid nitrogen surrounding the sample cell was removed. The integrator count was noted. The instrument was calibrated by mixing a known volume of adsorbate in the gas stream and recording the counts. The change in the composition of the gas stream flowing through the sample cell is sensed by a specially designed thermal
conductivity bridge. The bridge compares the thermal conductivity of the flowing gas before and after the sample cell. The difference is converted into Gaussian shape signals by means of an electronic circuit. The total area under the signal-time curve is proportional to the quantity of gas desorbed. The specific surface area was calculated as below.

The modified BET equation is

\[ X_m = X \left( \frac{P_o - P}{P_o} \right) \]

Where \( X \) is the weight of gas adsorbed at a particular relative pressure.

\( \frac{P}{P_o} \) is the relative pressure

\( p \) is the adsorbate pressure

\( P_o \) is the saturated equilibrium vapour pressure of the adsorbate at the temperature of measurement.

\( X_m \) is the weight of the gas adsorbed for mono molecular layer formation

\[ X = \left( \frac{A}{A_{cal}} \right) V_{cal} \left( \frac{P_a M}{R T} \right) \]

Where \( A \) is sample integrator counts

\( A_{cal} \) is calibration integrator counts
$V_{cal}$ is volume of adsorbate in calibration mixture.

$P_a$ is ambient pressure

$M$ is adsorbate molecular weight

$T$ is temperature in Kelvin.

$R$ is gas constant (82.06 ml. atm. deg$^{-1}$ mol$^{-1}$)

Total surface area $S_t = \left( \frac{X m N A_{cs}}{M} \right)$

$N$ is the Avogadro Number

$(6.023 \times 10^{23})$

$A_{cs}$ is cross sectional area of adsorbate nitrogen

$(16.2 \times 10^{-20} \text{ m}^2)$

Specific surface area $S = \frac{S_t}{\text{Weight of sample}}$

The data on specific surface area as determined during particle size analyses using Malvern Particle size Analyser were also furnished for all the samples (represented in m$^2$/cc) for comparison.

2.12 Determination of Density

Density for various lignite samples were measured using water displacement method which is reported to be best suited for brown coals. With salty lignites minor errors
could be caused by dissolution of soluble minerals in the water. Bed moist lignite was used whose moisture content was determined in a parallel test.

The solid density was calculated using the equation.

\[ d_s = \frac{d_{wp} d_w}{(m d_w + d_w - m d_{wp})} \]

where \( d_s \) is the solid density

\( d_{wp} \) is the measured particle density of the saturated coal.

\( m \) is the moisture content

and \( d_w \) is the density of water.


The pore volume distribution in lignites changes as they are treated hydrothermally. A brief study was made to compare the pore volume distribution of the raw and hydrothermally treated Neyveli (Mine I) lignites at different temperatures and corresponding pressures. The equipment used was MERCURY POROSIMETER 2000 SERIES, CARLO ELBA make, WITH MILESTONE 200 SOFTWARE.

A pre-weighed sample was placed inside the glass dilatometer. Then, the dilatometer was evacuated using DUPLEX MERCURY FILLING DEVICE. After the sample had been
degassed, the dilatometer was filled with mercury under dynamic vacuum conditions, by which the vacuum evacuation could be maintained during mercury filling process, thus eliminating any residual gases. The dilatometer was returned to atmospheric pressure after it had been filled with mercury. The dilatometer containing the sample and filled with mercury was placed inside the autoclave. The necessary pressure in the autoclave was achieved by a pressure multiplier consisting of a differential system with two pistons, a low pressure and a high pressure piston set to a pressuring ratio of 1:100. The low pressure piston was actuated by a low pressure oil drawn from a reservoir by the pump. The high pressure piston transferred the pressure to the mercury inside the dilatometer through a special dielectric oil as intermediate hydraulic fluid drawn from reservoir.

The monitoring system was based on the variation of the mercury level in the calibrated stem of the dilatometer. The progress of the penetration of the mercury into the sample was electrically followed by means of a patented capacitance system. When the pressure increased, the level of mercury in the stem fell and consequently the capacitance changed. This variation was electronically processed by the control unit and registered on the Data System used. When the autoclave
reached the maximum pressure set on the control unit, the system automatically started a decreasing pressure cycle.

The height of mercury column was detected and recorded at an interval of 0.1 mm, which corresponded to a pore volume increment of $7.07 \times 10^{-14} \text{ cm}^3$. In calculating the pore radius, the surface tension and contact angle of mercury were assumed to be 0.48 Nm$^{-1}$ and 140$^\circ$ respectively. It is reported by Gan et al.$^{72}$, that in the case of anthracite sample, 60 psi is sufficient to fill the voids and any further mercury penetration at higher pressures will be due to the presence of pores.

During several trial runs, no change in the height of mercury column was detected beyond 500 psi pressure, with respect to Neyveli(Mine I) lignite samples Hence a maximum pressure of 500 psi was applied in all the test runs.

2.14 Preparation of Lignite-Water Slurries

The slurry samples required for the rheological studies were prepared as follows:

A weighed quantity of demineralized water was taken in a beaker. Weighed quantity of prepared lignite sample was added in small increments to the beaker containing water and the mixture was stirred manually using a glass rod. After
Fig. 2.3  Schematic of Haake RV20 Viscometer System.

Fig. 2.3.1 Photograph of Haake RV20 Viscometer System.
all the lignite samples were transferred as above while stirring, the mixture was blended using a Remi paddle-type stirrer at 500 RPM, for exactly 1 minute. As all the lignite water slurries were found to be shear-thinning, the above period of mixing was maintained the same, during the preparation of all slurry samples to get reproducible viscometer outputs, for comparing the rheological characteristics of various lignite-water slurries. Each time, 100 g of the lignite-water slurry was prepared taking care that air bubbles were completely removed during slurry preparation.

2.15 Determination of Apparent Viscosity, Slurriability, and Rheological Characteristics.

The rheological properties of the lignite-water slurries produced, which in general behaved as non-Newtonian fluids, were measured using HAAKE RV 20 ROTOVISCO VISCOMETER SYSTEM consisting of Measuring system M5, Rheocontroller RC 20, connected to an IBM Computer with a printer, Coaxial cylinder sensor system (profiled cup MVP and profiled rotor MV2P) and Hake constant temperature liquid circulator. A simplified drawing and a photograph of the unit are shown in Figs. 2.3 and 2.3.1 respectively. A cooling/heating jacket was provided around the coaxial cylinder sensor system. The
thermal liquid circulator connected to the above jacket consisted of a built-in refrigeration and heating facility. This was used to maintain a temperature of 25° during the measurement. The measuring system M5 was limited to measuring an upper shear stress of about 376 Pa when using MV series spindles, and an upper shear rate of 451 s⁻¹.

About 55 ml of the prepared sample of lignite-water slurry was immediately placed between the two coaxial cylinders of the sensor unit and inner cylinder (rotor) was rotated by the mechanical drive. The torque, caused by the resistance of the sample to shearing, was determined by measuring the distortion of a calibration spring.

The spring deflection was transformed into an electrical signal which was recorded.

The lignite loadings for the various slurries were determined by ASTM D3173 moisture analysis method.

2.15.1. Determination of Slurriability

Lignite - water slurries of different solid loadings were prepared. The above samples were subjected to a constant shear rate according to the following viscometer conditions.
1. Shear rate .... $100 \text{ s}^{-1}$ (constant)

2. Period of shear .... 15 s

3. Temperature .... $25^\circ$

4. Number of steps (set of readings to be noted within 15 min. .... 100

Several tests (more than 4) at increasing solid loadings were run until a viscosity greater than 600 cP was measured at the above conditions. Each time, the apparent viscosity values were noted after 50 seconds of constant shear rate at $100 \text{ s}^{-1}$. This was justified on the fact that all the lignite-water slurries tested were shear thinning in nature and the point at 50$^{th}$ second falls on the linear portion of the viscosity - time curve after the initial turbulence due to overcoming the yield stress. Further, the viscosity value at 50$^{th}$ second will provide data for comparing and plotting viscosity values for different lignite water slurries all of them being shear thinning. Interpolation between the solids loading and apparent viscosities was done to determine the solids loading that corresponds to 600 cP.

The apparent viscosity at $100 \text{ s}^{-1}$ was calculated as below:
\[ \eta \text{ (in centipoise)} = \frac{\tau_s}{D_s} \left( \frac{\% \tau}{\% D} \right) \times 10^3 \]

Where \( \tau_s \) = shear stress at 50th second

\[ D_s = 100 \text{ s}^{-1} \]

\( \% \tau \) & \( \% D \) (Scale gradients) = 100

Factor A (Pa \%) = 3.76

Factor M (s\(^{-1}\) / \% D) = 4.51

The factors A and M are understood as below:

**Shear Rate**:

For coaxial cylinder sensor systems, the shear rate at the inner cylinder (rotor) is given by:

\[ D_i = 2 \omega \frac{Ra^2}{Ra^2 - Ri^2} \]

\[ \omega = \frac{2 \pi n}{60} \]

\[ D_i = \left\{ \frac{\pi}{15}, \frac{Ra^2}{Ra^2 - Ri^2} \right\} n \]

\[ Di = M \cdot n \text{ (s}^{-1} \text{)} \]

Where \( D_i \) = Shear rate (s\(^{-1}\)) at rotor radius \( R_i \)

\[ \omega = \text{angular velocity (s}^{-1} \text{)} \]

\[ Ra = \text{Radius of the cup (cm)} \]
\[ R_i = \text{Radius of the rotor (cm)} \]

\[ n = \text{Rotor speed (min}^{-1}\text{)} \]

\[ M = \text{Shear rate factor (s}^{-1}\text{/scale grad)} \]

It combines all factors given in the above bracket \{ \}. ie it depends on the radii of the cup and the rotor.

\[ M = 4.51 \]

The shear rate at the rotor surface equals the rotor speed \( n \) multiplied by a constant "\( M \)" which depends on the radii of cup and rotor of the particular sensor system.

**Shear stress:**

\[ \tau_i = \frac{M d}{2\pi \cdot h \cdot R_i^2} = \left\{ \frac{1}{2\pi \cdot h \cdot R_i^2} \right\} M d \quad \text{(1)} \]

\[ \tau_i = f \cdot M d \]

\[ \tau_a = \frac{M d}{2\pi \cdot h \cdot R_a^2} \]

\[ \tau_r = \frac{M d}{2\pi \cdot h \cdot n^2} \]

\( \tau_i \) = Shear stress at the radius \( R_i \) (Pa)

\( \tau_a \) = Shear stress at the radius \( R_a \) (Pa)
\( \tau_r = \) Shear stress at the radial coordinate \( r \) (Pa)

\( M_d = \) Torque to be measured (N.cm)

\( h = \) Rotor height (cm)

\( f = \) Shape factor (cm\(^3\)). It combines all the factors in the above bracket \( \{ \} \). It is a constant for a particular sensor system defining the geometry of the rotor.

The evaluation requires the knowledge of \( \tau_i \) and \( \tau_r \) while \( \tau_a \) is, for most tests, less important.

If the mechanical torque \( M_d \) determined by the torque sensor is transformed into an indicator signal \( S \) being displayed on the indicating part of the viscometer system, equation 1 may be rewritten as:

\[
\tau_i = f \cdot \frac{M_d}{S} \cdot S \quad a = \frac{M_d}{S} \quad (\text{N. Cm} / \text{Scale Gradient}) 
\]

\[
\tau_i = f \cdot a \cdot S \quad A = f \cdot a \quad (\text{Pa} / \text{Scale gradient}) 
\]

\[
\tau_i = A \cdot S 
\]

The constant "a" defines the linear relationship between torques on the rotor and the corresponding "S" - signals displayed. Combining the constant "f" and "a" leads to a shear stress factor "A" which is a constant for a particular
sensor system and its viscometer. The value of "A" is given as 3.76 Pa/% in the instruction manual.

The shear stress in is therefore defined by the measured "s" signal, multiplied by the relevant constant shear stress factor "A".

2.15.2 Determination of Rheological Characteristics

The flow curves viz. plot of shear stress against shear rate for the specified lignite - water slurries (both raw and treated) were obtained as per the following viscometer conditions:

1. Shear rate : 150 s⁻¹ (Max)

2. Period of shear : 5 min.

3. Steps (set of readings to be noted within 5 min.) : 100

The test was to measure shear stress of the slurry continuously with linearly increasing shear rate, the variation of the shear rate being controlled by the microprocessor. The shear rate was increased linearly from zero to 150 s⁻¹ in a period of 5 min. The "Yield stress"
(Shear stress at zero shear rate) was determined from a log-log plot of shear stress against shear rate and subsequent extrapolation of the straight line to cut y axis. The equation corresponding to the non-Newtonian flow curve was obtained for each test-run with each sample of lignite water slurry, as follows:

The computer was fed with 20 to 50 pairs of (shear stress) and D (shear rate) stored during a rotational viscometer test. A check was made by the computer mathematically up to 10 different mathematical models and a particular model was selected along with its specific coefficients which when plotted would give the "best fit" to the flow curve.

Some model equations to fit flow or viscosity curves are as below:

Linear : \( Y = a + b \times X \)
Linear reciprocal : \( Y = \frac{1}{a + b \times X} \)
Exponential : \( Y = a \times e^{b \times x} \)
Linear (Newton) equation : \( \tau = \eta D \)
Power law equation : \( \tau = K \times D^n \)
Herschel Bulkley equation : \( \tau = \tau_0 + K \times D^n \)
Logarithmic equation : \( y = a + b \times \log x \)
Hyperbolic equation: \( Y = a + \left( \frac{b}{X} \right) \)

Bingham plastic equation: \( \tau = \tau_0 + \eta D \)

Casson equation: \( \sqrt{\tau} - \sqrt{\tau_0} = \sqrt{\eta} \times D \)

Since any equation can give an acceptable approximation of the real flow curve within certain shear rate ranges only; limits were chosen in the real flow curve before regression analysis and no attempt was made to extrapolate beyond the limits chosen. The approximation was considered to be good enough when the regression factor was \( R^2 = 0.99 \) to 1.0. The coefficients of the best fit equation give the values of flow consistency number and flow behavior index \( n \). The extent to which the flow behavior index deviates from 1.0 determines the degree of non-Newtonianism.

In all the tests with different lignite samples, the solid loadings of the lignite-water slurry was fixed as 45% by weight. This is to enable best comparison between different lignite-water slurries.

2.15.3 Study on Thixotropic Characteristics

The thixotropy of lignite-water slurries is caused by the network structure formed between the lignite surface and water. An attempt was made to investigate the thixotropy
of raw and hydothermally treated lignite - water slurries using "Hysteresis Loop Method". In this method the measurement of shear stress was made with linear increase of shear rate from zero to 150 s\(^{-1}\) and then the shear rate was decreased to zero, the measurement of shear stress being continued. The shear cycle was repeated twice or thrice depending on the type of lignite used. These curves mutually connected with the head to the tail form a "screw curve". The shear test was continued until these curves form closed equilibrium loop. The area of the loop was used as a measure of the degree of thixotropy. The conditions of the viscometer used are given below:

<table>
<thead>
<tr>
<th>SHEAR CYCLE</th>
<th>TEMP °C</th>
<th>SHEAR RATE s(^{-1})</th>
<th>PERIOD min.</th>
<th>STEPS (SETS OF READINGS TO BE NOTED)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>25</td>
<td>0 - 150</td>
<td>2.5</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>150 - 0</td>
<td>2.5</td>
<td>100</td>
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<tr>
<td>2.</td>
<td>25</td>
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</tr>
<tr>
<td></td>
<td>25</td>
<td>150 - 0</td>
<td>2.5</td>
<td>100</td>
</tr>
<tr>
<td>3.</td>
<td>25</td>
<td>0 - 150</td>
<td>2.5</td>
<td>100</td>
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<tr>
<td></td>
<td>25</td>
<td>150 - 0</td>
<td>2.5</td>
<td>100</td>
</tr>
</tbody>
</table>
2.15.4 Study of Variation of Shear Stress with Time

Variations of shear stress with time for raw and hydrothermally treated lignite were studied at three different constant shear rates viz., 50, 100 and 150 s\(^{-1}\).

The conditions of the viscometer were:

1. Temperature : 25\(^\circ\)
2. Shear rate : 50 / 100 / 150 s\(^{-1}\) (constant)
3. Period : 15 min.
4. Steps (Number of set of readings to be noted) : 100

The viscosity was then plotted vs \(\ln t\). It is reported \(^7\) that the viscosity loss is linear with logarithmic time until the equilibrium state is reached. If this is done at a series of arbitrary top shear rates, then a family of parallel straight lines are obtained Green and Weltmann \(^5\) characterized the slope of these parallel lines \(d\eta/d\ln t\) by the symbol \(B\) and called it the "Coefficient of thixotropic break down with time"

The values of \(B\) for different raw and treated lignites were determined and compared.

The data obtained by these tests are to validate the area of the hysteresis loops obtained in the earlier test runs.
2.17 Determination of Stability of Lignite-Water Slurries

Stability of lignite-water slurries was determined from the extent of settling after prefixed time, and expressed as concentration of lignite in upper half of lignite-water slurry with respect to the initial concentration of LWS system taken in a measuring cylinder under standard condition. The measuring cylinder has 100 mm dia and 400 mm height. The sample from the cylinder was carefully taken out with a specially fabricated spatula with minimum possible disturbance to the remaining part of LWS. The stability was calculated as follows. Stability % = [Concentration of lignite in LWS (in upper half of cylinder) after prefixed time]/[Initial concentration of lignite in LWS] X 100.

The concentration of lignite was determined gravimetrically by drying the LWS sample in an oven under standard conditions. A critical review of various methods available was made by Electric Power Research Institute (EPRI)\textsuperscript{75-A}

The softness of pack of the settled mass gives an indication of its repulpability. It was measured by RO\textsuperscript{OD PENETRATION TEST}\textsuperscript{76} and calculated as follows:
Softness of pack

\[ \text{Softness of pack} = \frac{\text{Length of the standard rod penetrated}}{\text{Total length of LWS column}} \times 100 \]

The slurry was placed, under room temperature in a cylinder and the stability of it was evaluated by measuring the volume of produced deposit and the penetrating time of the rod every week.

2.18 Petrographic Analysis of Lignites

The extent of hydrophobicity attained by lignite during hydrothermal treatment depends on the nature of organics present in it. The petrological analysis of raw and hydrothermally treated lignites was done to understand the changes in the microscopically distinguishable macerals and also to make gross predictions regarding the behaviour of certain lignites during hydrothermal treatment.

Lignite contains components including plant remains derived from ligno-cellulosic tissue, spores, resins, cuticles, and waxes. These materials decayed and gellified to varying degrees. Ultimately they became compacted and under the influence of elevated temperature associated with burial within the earth crust, they advanced in maturity and achieved this present level of rank. The status of this
maturity of different macerals differ from even lignite to lignite which makes the behaviour of a lignite towards hydrothermal treatment so specific and subsequently the products also differ from each other in physical and chemical properties.

These different plant derived materials in lignite have been microscopically identified and categorized and are referred to as macerals. The nomenclature used herein to categorize macerals corresponds approximately to that outlined in 1976 by the International Committee for Coal Petrology for Low Rank Coals.

The three maceral groups are:

1. **Huminite** (The vitrinite of low rank coals) which includes Ulminite, Humodetrinite, Gelinite, and Corpohuminite

2. **Liptinite** which includes Sporinite, Resinite, Cutinite, Suberinite and Liptodetrinite.

3. **Inertinite** which includes Fusinite, Semi inertinite (including Semi-fusinite, some Semi macrinite, and some Sclerotinite), Macrinite, Scloridinite, and Inertodetrinite.

The huminite portion of the maceral exhibits plastic properties upon heating resulting in volumetric changes. During the natural
process of coal formation, the huminite portion of the maceral, gets compressed with age thus resulting in reduced volume moisture, surface area, porosity and increased carbon content.

Within the lignite rank itself, depending on the conditions to which the cellulose structures are subjected to humification, changes in huminite levels are expected. Accordingly the behaviour of lignites towards hydrothermal treatment also may vary.

Huminite looks grey in reflected light under the microscope and the % reflectance varies from one lignite sample to other. The liptinites(exinites) have typically lower reflectance and auto- fluorescent property, a high hydrogen content and higher proportion of volatile matter than the vitrinites. Liptinites are recognized by their fluorescence in UV light due to the hydrogen content.

Inertinite (Fusinite) has the higher reflectance of all macerals. Fusinite is a non plastic constituent with very low porosity. it commonly displays residual cell wall structure.
Sample Preparation for Microscopic View:

The lignite was hand crushed and the throughput was sieved with a 20 mesh (850 mm) screen. The over size material was crushed and sieved again until all of it passed through 20 mesh screen. Five to six stages of crushing were required in order to generate minimum amounts of fines (less than 40 m). The crushed lignite was then mixed with an epoxy resin (araldite bonding agent with hardener) mixture in the ratio of about 4 parts of lignite to one part of epoxy resin by volume, thoroughly mixed and filled into a cylindrical steel mould 4 cm in diameter.

The lignite-epoxy mixture was then briquetted under a pressure of approximately 350 kg/cm\(^2\) for 2 min. A releasing agent was used to avoid bonding of the briquette to the mould.

The briquette was then allowed to cure in the mould overnight. The briquette was ground successively with 240-, 400-, and 600- grit silicon carbide paper and 5.0 and 0.3 m alumina on synthetic cloth and 0.05 m alumina on silk\(^7\). The polished briquettes were preserved in a desiccator.
Fig. 2.4  Photograph of Leitz Orthoplan- Pol microscope.
Instrumentation

The microscope used for the petrological studies of lignites is the LEITZ ORTHOPLAN-POL with its accessories viz, MPV micro photometer, "Vario Orthomat" photomicrographic system, "Pleomopk" fluorescence vertical illuminator, and swift automatic point counter. (Fig.2.4)

Maceral Counting:

One of the eyepieces of the microscope is fitted with a cross wire to serve as a reference for selecting specific locations on the polished surface. The microscope is also fitted with a stage that permits moving the sample by fixed increments in two perpendicular directions. The observer has to identify the constituent every time the specimen is stationary under the cross lines, and press the appropriate channel key. Every time a key is pressed, the specimen moves one step in the horizontal direction. At the same time one count is added to that particular channel as well as to the memory of the total count. Counting is continued until a pre-set total has been reached and an audible alarm is also given.
**Microscopic Arrangements:**

Pellet is placed on the microscope stage and the incident light microscopic adjustments were done. The pellet was placed on the "stepping stage" which was electrically operated and controlled by the Swift point counter.

NPL 20x / 0.45 objective with 10x eyepiece was used. The magnifications were chosen as per the experimental requirements.

**Point Counter Arrangements:**

The total count was set for 500 as per ASTM standard. But during the measurements, countings beyond 100 become redundant since the sequence of the macerals are getting repeated systematically for each set of 100 countings for all samples investigated. The stepping stage movement was set up at fourth position. The first five keys were selected and labelled with the maceral names. The counter is pre-set. Also, the 12th channel was isolated and labelled as mineral matter.

**Reflectance Analysis:**

Reflectance may be defined as the proportion of normally incident light that is reflected by the specimen. It is usually expressed as a percentage, so that reflectance of 1.00% for vitrinite indicates that only that proportion of the light incident on coal surface is reflected.
2.19 Infrared Spectrophotometric Studies

Transmission infrared red spectra of Neyveli raw and hydrothermally treated lignites were recorded between 4000 and 200 cm$^{-1}$ with a Perkin Elmer Grating Spectrophotometer with a resolution of about 4 cm$^{-1}$. The lignite samples were dried at 105° for 4 h in an air oven prior to spectroscopic examination in a current of nitrogen. 3 mg of dried lignite sample was mixed with 100 mg of KBr and a pellet was made which was spectroscopically examined.

The concentration of the lignite in the pellet, the pressure applied to make the pellet, the spectrophotometer setting parameters were kept the same for all lignite samples to achieve a quantitative comparison of changes in functional groups and degree of hydration.

2.20 Study on the Physical Morphology

A Scanning Electron Microscope, JEOL make, and JSM-35 CF model was used to examine the physical morphology of the lignites before and after hydrothermal treatment, at various magnifications for the purpose of comparison. Prior to microscopic viewing, the lignite particles were mounted on a tape with an adhesive and were coated with gold using JEOL, FINE COAT ION SPUTTERING EQUIPMENT MODEL JFC 1100 at 1.5 KVA and 6-7 mA current.
Fig. 3.1 PREPARATION AND ANALYSIS SCHEME FOR RAW LIGNITES