CHAPTER-III

EXPERIMENTAL INVESTIGATION

INTRODUCTION:

The rock samples used in this study and their analysis with various equipments are given. The preparation of rock sample solution, details of various chemicals used and procedure adopted for doing the tests, for estimating the fixed carbon and calculation of various parameters are all summarized in this chapter. Various laboratory techniques XRD analysis technique, Differential Thermal Analysis (DTA), Wavelength Dispersive X-ray Fluorescence Spectrometer, Atomic Absorption Spectrophotometer (AAS), Scanning Electron Microscope etc., used for the determination of whole rock mineralogy of graphite were applied to extract requisite information out of the collected rock formation samples by analysis and interpretation. The existing methods for sampling collection and processing are used to assess the particle size, and fixed carbon content in the collected samples. The available information on history of graphite based on the detailed studies carried out so far will be used for analysis of the experimental results obtained.

3.1 COLLECTION OF SAMPLES:

Vizianagaram, Visakhapatnam, East Godavari and Khammam geographical regions which cover 1947.07 sqkm are deposited with graphite ores. For easy consideration of geochemical, mineralogical and mineral processing studies, representative bulk samples (50Kg) were collected from each of the selected locations.
Sixteen locations namely Vizianagaram, Nandakota, Gummakota, Marupalle, Kondamusuru, Kokkirapalle, Pydipala, Shivalingapuram, Pasappadu, Sada, Burugubanda, Utla, Sitapalli, Pydiputta, Tapaskonda, and Jeediguppa were selected for detailed geological investigation and sampling of graphite minerals, ores and other associated rocks. The samples of graphite ores and the associated rocks were collected from the localities on the basis of degree of graphite mineralization in the horizons of the metamorphic rocks. Due consideration was given to the geological setting of graphite mineralization in the khondalite sequence.

The sampling was done along a profile across the graphite lenses in such a way that the overlying and underlying Khondallite suites of rocks were also covered. The mineralized lenses of graphite were further considered for detailed sampling within the lens so that mineralogical changes and the geochemistry of graphite minerals could be investigated in detail. Due to hard and compact nature of the rocks associated with graphite lenses, the samples were collected either by cutting. Samples were also collected from abandoned mines and the mines in operation. The samples from some mines show very good relationship between the are body and the host rocks and thus provided better condition of sample collection with respect to the associated rocks and also within the graphite lenses.

On 150 graphite bearing samples which represents oxides, silicates and litho units, petrographic, mineralogical and trace elemental studies were carried out. Using optical methods adopting thin sections petrographic studies of 50 associated rock samples were carried out.
3.2 LABORATORY STUDIES

3.2.1 PETROGRAPHIC STUDIES:

The petrographic studies include mineral composition, grain and sediment Province, fabric studies and determination of the sequence of diagenetic events (Tucker, 1988). All the collected samples in the field were recorded in a register in systematic manner for further utilization and interpretation. A chip of appropriate size was cut from representative samples by rock cutter for the preparation of thin sections under trinocular ore microscope.

3.2.2 X-RAY DIFFRACTION

The x-ray diffraction falls under the modern tools. It is a basic tool in the mineralogical analysis of sediments especially in the case of fine grained sediments. XRD has the advantage with modern instrumentation in which almost complete automation can be achieved to give fast and precise results with respect to mineralogical analysis. The XRD analysis technique was applied for the determination of whole rock mineralogy of graphite. The selected rock samples were prepared according to the standard procedure and were subjected to XRD analysis at RSIC, Nagpur. The powder diffraction patterns of X-ray analysis of graphite and associated minerals were obtained from Philips X-ray diffractometer using Cu Kα radiation target with scanning speed 5mm/deg and 2θ of 0°- 90°.

3.2.3 DIFFERENTIAL THERMAL ANALYSIS STUDIES

Graph pattern of Differential Thermal Analysis (DTA) of graphite samples were obtained with heating rate of 20°C/Min chart speed 300mm/hour sensitive of 50uv using the Al₂O₃ reference standard on 673
model differential Thermal Analyzer at Instrumentation center, Andhra University, Visakhapatnam.

3.2.4 MAJOR ELEMENTAL ANALYSIS

Major elements were determined by Wavelength Dispersive X-ray Fluorescence Spectrometer (WDXRFS) at Steel Plant, Visakhapatnam. 0.5mg sample powder of 230# is mixed with 5gm Sodium Tetra Borate and fused at 1300\(^0\) C in a Furnace to prepare a sample for the analysis.

Minor

3.2.5 MINOR AND TRACE ELEMENTAL ANALYSIS

Minor and trace elemental analysis of the samples was performed with Perkin Elmer 2380 Atomic Absorption Spectrophotometer (AAS) in our Department of Environmental studies, GITAM, Visakhapatnam using Acetylene and Nitrous oxide as burning fuels.

The graphite sample and graphite separated sample was subjected to (JEOL JSM-T330-A) Wavelength Dispersive Spectrophotometer X-ray counting system (WDS-XRCS) attached to Scanning Electron Microscope (SEM), at Andhra University, Visakhapatnam. WDS is employed on four crystal spectrometer which is capable of analyzing B\(_5\) (Boron) to U\(_{92}\) (Uranium) with excellent wavelength resolution and high sensitivity. The XCS compact X-ray counting system developed exclusively incorporates a spectrometer controller, a counter, a chart recorder etc.

Chemical analyses for Trace elements were conducted using Inductively Coupled Plasma Spectrophotometry (ICP-MS) method at National Geophysical Research Institute (NGRI), Hyderabad.
The ICP-Mass Spectrometer has proved to be a versatile and powerful
technique for handling the routine analytical problems involving both
elemental and isotopic analysis in a wide variety of matrices. The instrument
used for the analysis is the Plasma quad (VG Elemental, Winsford, UK)
controlled by IBM PC – XT Computer. The ICP torch is of fassel design,
sample and skimmer cones are fabricated from high purity Nickel.

The instrumental parameters were kept constant through out the
analysis. The following isotopes were used in the analytical determinations
are Sc, V, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Ba, La, Ce, Pr, Nd, Sm, Eu,
Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta. Single isotopes were used for all
elements. The isotopes were selected taking into consideration of their effects
by other elements present in the rock samples. Some isotopes such as Sc are
mono isotopic and thus no choice is available.

Spectroscopic grade aqueous metal solutions and high purity double
distilled water was used for the preparation of synthetic multi element
standards. The acids used were of analytical grade.

The multi element solutions were obtained from Spex industries (USA).
To prepare a 100mg/ml multi element standard, appropriate volume of the
above solutions, including the internal standard indium was transferred into I-
L polypropylene volumetric distilled water. An overall acidity of 5% was
maintained with respect to Nitric acid.

Some of the samples were analyzed using Inductively Coupled Plasma-
Atomic Emission Spectrometry at Canada. ICP-AES is being used increasingly
for the analysis of a wide range of geological materials. The rapidity of these
multielement techniques results in sample dissolution by two routinely used
sample preparation methods. LiBO₂ (Lithium metaborate fusion and open
vessel HF-HClO₄ digestion and reded vessel acid digestion for materials containing refractory minerals of Zircon, Tungsten, Chromium etc., combination of these method proved better sample preparation. These methods were adopted by Potts (1987), Moore (1989), Thompson and Walsh (1989), Jarvis and Jarvis (1992).

Tungsten is estimated by Color intensity produced by the tungsten present in the sample is compared with the standard tungsten solutions ranging from colorless(zero) through increasing intensities of blue-green covers the range 4-400ppm which may be extended up to 2000ppm using the method suggested by Stanton (1966).

3.3 GRAPHITE PROCESSING

There are different grades of graphites which are associated with varied gangue minerals in which few are valuable, needed recovery in different geographical regions. To bring out a marketable grade for different industries, all these types of graphites are to be processed so that the gangue minerals are removed by different operations to obtain high content of graphite concentrates have to be obtained.

3.3.1 PROCESSING METHODOLOGY:

By using Jaw crusher, the samples were crushed to ¼ inch and then subjected to Ball mill and then to Decantation cell for getting finer size. Using ASTM meshes -45+60, -60+80, -80+100, -100+120, -120+200, -200 the ground material was subjected to size analysis. Using different reagents for getting maximum recovery and also to recover tungsten minerals (as by-product) by adopting suitable gravity separation methods like jigging, tabling and hydro cyclones depending upon the size of the material, each fraction
was subjected to floatation tests carried out by Denver Sub ‘A’ flotation cell of 1Kg capacity.

### 3.3.2 VARIOUS STAGES OF PROCESSING

1. **a. primary crushing:** After blasting the ore at site, this was done using primary breakers and crushers. From 6Ocms to 5cms the ore was reduced.
   
   **b. Secondary crushing:** For reducing from 5cms to 0.25cms which suit for grinding to fine sizes of 0.25cms to 0.1mm, This was done by Gyrator crushers, crushing rolls etc.

2. **Sizing:** To give definite size to suit the grinding machines, the crushed ore was subjected to screening by vibrating and gyratory screens before subjecting to grinding.

3. **Grinding operation:** By adopting swing hammer mills and roll crushers, fine grinding is always avoid such that to recover the coarse flaky material. Depending upon the type of ore which contains coarse flaky — graphite to some extent, the introduction of these two types of machines in the circuit was done. rod mills are used and in the case of medium flaky ore to grind the material at optimum conditions, fine flaky ore and ball mills and tube mills are used.

4) To recover the wolframate and scheelite which are cause and higher specific gravity materials. To recover graphite from gangue minerals, the sized material coarse, fine and medium size were subjected to different operations where higher specific gravity minerals by (a) Flotation (b) Tabling and (c) Jigging process.
3.4 FLOTATION PROCESS

On introducing air bubbles into properly prepared pulp properly or suspension of finely pulverized ore in water, certain minerals particles will adhere to the air bubbles. This tendency is not shown by other mineral particles and they remain suspended in water separately. Pulps carry the rising out air bubbles along with them. By suitable mechanical means, particles may be removed as a “concentrate” of one of the mineral group forming mineral froth layer. The tendency of particles of that mineral to adhere to air bubble is determined by the floatability of that mineral. Specific gravity and other purely physical properties of the mineral play little part in flotation.

The flotation process are controlled by some chemical properties control namely
(a) Wettable and non-wettable polar molecules are made up of ions Na⁺ Cl⁻ Na⁺ Cl⁻.
(b) Paraffin’s, hydrocarbons CₙH₂n₊₁ are chemical structural arrangement in which non-polar molecules are atom with no evidence of any of those chemical structural arrangements. These are non-wettable hence flotable.

Keeping part in contact with air phase & remaining part in contact with water phase, each non-wettable or each floatable particles tend to become attached to a bubble surface. The inter sect of three surfaces like air-water, air-solid, water-solid will lead to the formation of line around a particle. The angle between the solid surface and the bubble surface measure in the liquid phase the contact angle. Water will tend to displace air at the solid surface if the contact angle is very small or ‘Zero’. Thus the minerals are non flotable and the surface is wettable.
The following procedure is adopted carryout floatation process. Generally wet grinding is adopted to get the product from the pulp whose density generally varies from 25-50%. The mineral matter is pulverized to fine powder generally -65mesh to 200mesh. For about 3 to 5 minutes in the grinding unit itself, the pulp is treated with flotation reagents by way of mixing in a conditioning tank. In the floatation cell, sub 'A' floatation cell type, This conditioned pulp is diluted and subjected to floatation process.

3.4.1 FLOTATION REAGENTS

(a) The chemicals that produce froth and stabilized froth are the Frother agents. In their molecule characterized by the presence of water ‘avid’ (liking) polar group and a water repellant ‘non-polar’ group (hydrocarbon group) they are organic chemicals. Cresylic acid, eucalyptus oil, camphor oil, sage brush oil, amyl alcohol, synthetic frothers Pine oil, like sulphonated alcohols.

(b) The chemicals that cause collection of the desired minerals in to the froth are called Collecting agents. With molecules containing both polar and non-polar parts, they are organic chemicals. Define reactive and pronounced tendency to ionize is shown by the polar parts of collector molecules. To the mineral particle surface, the active polar groups serve as a means of adhesion of a film or coating. For bubble attachment and floatation, the non-polar Hydrocarbon group gives thin Surface film or coating is non-wettable or water repellant properties necessary. Thio carbonilides, fatty acids, stearic acid, palmitic acid, coal tar creosotes, wood tar creosotes, petroleum product Amyl xanthate, dithio phosphates, etc.

(c) Modifying agents: are used in selective or differential floatation. They are pH controller (Acid medium or alkaline medium), Depressing agents activating
agents, and Sulphidising agents. Dispersing agents (defloculant, protective colloids).

By adding Acid, Sodium carbonate, to maintain necessary pH. The three mediums are Acid, Neutral, Alkaline media controlled. Inorganic chemicals which react chemically or surface adsorption depressing agents. By commonly used collectors activating agents are certain minerals particularly sphalerite and some non metallic minerals in their natural state are not collected. To cause the collection and also to bring about flotation activating agents are used (example copper sulphate to activate sphalerite).

Oxidized minerals and metallic oxides and may be flotable by adding sulphidising agents. Poly sulphides, Sodium sulphide and hydrogen sulphide.

The solid particles with non-wettable surfaces, non-polar in general will show pronounced tendency to floculate where as polar wettable particles trend to disperse are dispersing agents. To prevent excessive contamination of silica in the concentrate. Sodium silicate is used as dispersing agent. Protective colloids like Startch, glue, citric acid, lactic acid which are known as are used as dispersing agents and depressing agents.

3.4.2 FLOTATION EXPERIMENTS OF GRAPHITES

With agitator froth types, Denver sub ’A’ type flotation cell was used. Graphites flotation from Easternghats. The graphite occurrences are divided into four geographical regions.

Using the following flotation reagents on different sizes namely - 45+60, -60+80, -80+100, -100+120, -120+200, -200 A.S.T.M meshes, from different geographical regions flotation tests were carried out on the graphite
materials from gangue minerals, liberation of graphite particles is different and is maximum in the finer sizes. Coarse sizes also show nearly complete liberation of graphite from gangue In the case of the coarse crystalline varieties of graphite.

Pine oil at different quantities is the frothers. Kerosene, Turpentine, Linoleic acid at different quantities are the collectors, Sodium silicate at different quantities are the depressors and Sodium carbonate, Sulphuric acid at different quantities are the pH controllers. The different reagent combinations are given below and the results are given.

Combination A: Pine oil – frother, Kerosene – collector, Sodium silicate – depressor, Sulphuric acid – pH controller
Combination B: Pine oil – frother, Kerosene – collector, Sodium silicate – depressor, Sodium carbonate – pH controller
Combination C: Pine oil – frother, Potassium ethyl xanthate – collector, Sodium silicate – depressor, Sodium carbonate – pH controller
Combination D: Pine oil – frother, Linoleic acid – collector, Sodium silicate – depressor, Sodium carbonate – pH controller
Combination E: Pine oil – frother, Turpentine – collector, Sodium silicate – depressor, Sulphuric acid – pH controller

In changing the reagents quantities, are and the resultant concentrates (froth) are collected and assayed for fixed carbon. The following deductions are made from the results of the experiments.

For depressant of silica and silicates from graphite Sodium silicate is extensively used. Quartz and pegmatites are generally associated with the Easternghats graphites. As depressant flotation tests were carried out to obtain higher and better grades of graphite using sodium silicate at 5 kg/ton
of graphite material, Sodium silicate is used. In single flotation, some times it also gives commercial grade of graphite flakes -45+60 size at 55.5% fixed carbon. One can get commercial grades of graphite concentrates in all size ranges.

Amongst reagents combination pine oil as frother (0.4kg/ton), Kerosene as collector (0.4kg/ton), Sodium silicate as depressor (4kg/ton), sodium carbonate 0.4kg/ton) as pH controller gave a best result with 76.5% fixed carbon with 92% recovery in a single flotation.

But the experiments using pine oil as frother (0.4kg/ ton) Kerosene as collector (0.4kg/ton), Sodium silicate as depressor (4kg/ton), Sulphuric acid (0.4kg/ton) as pH controller gave a higher grade of graphite namely 78.5% fixed carbon but with lower percentage of recovery namely 63% fixed carbon.

Pine oil, kerosene, sodium silicate, alkaline pH flotation test is the best combination at - 120 mesh where there is generally complete liberation of graphite material from different geographical regions is summarized.

3.5 Summary:

This study also requires the knowledge of trace element association with the graphite ore deposits. The trace elements association is one of the criteria to know the grade, quality of graphite content. Further these trace elements availability in the graphite deposits results rate of grade of graphite with age factor including texture, and structure of the formation. To know the grade of graphite deposits, the concentration of index trace element range is playing effective role, which reflects the gradation of graphite on parallel with trace element concentration has to be used in determining the grade of graphite. Higher the index trace element availability indicates high grade
graphite deposits. The best way to detect graphite grade by analyzing the associative index trace element quantity in the samples. In this study it is proposed that trace element geochemical study reveals that its associated mineral concentration is directly proportional to grade of graphite i.e higher number of associated minerals indicates high grade of graphite availability in youngest Archean formations in medium to coarse grained texture with high tectonic activity. Less number of associated minerals with low grade graphite availability in oldest formation in fine to medium grained texture with less tectonic activity at high altitudes and at places of plain areas. This prediction has to be established by applying above trace element association with graphite deposit in khondallite formation. The association of trace element with graphite samples analysis has been done in the laboratory and determined the relation of trace element versus graphite deposits. However the comparison process is not a simple but different methods applied for it.

Trace element association with graphite availability shows special way to identify the concentration of carbon content with high grade material. Low carbon group of minerals along the Easternghats from east to western boundary of the study area. The youngest Khondalite suite of rocks showing with medium to high grade carbon availability. The radiation effect of these minerals in the study area resulting precious quartz group of minerals like cats eye, Alexandrite, Moon stone etc. which are highly valuable in jewelry industry. Hence, the gangue material soon after recovery of carbon content is very useful and the disposal pattern of the gangue is also eco friendly without any environmental impact in the area. Index trace elements are categorized in to three types as per the association with carbon content.