

Industrial Suitability of Recent Coastal Sands of Ilmenite, Rutile, Garnet and Monazites of Gosthani and Champavathi River Confluences, Andhra Pradesh, East Coast of India

K.Bangaku Naidu^{*1}, K.S.N.Reddy², M.Anji Reddy¹

^{*1}Center for Environment, Jawaharlal Nehru Technology University Hyderabad, Telangana, India

²Department of Geology, Andhra University, Visakhapatnam, Andhra Pradesh, India

ABSTRACT

Geochemical studies of ilmenite, rutile, garnet and monazite grains by using Electron Micro Probe Analysis (EPMA) from coastal sands of Gosthani and Champavathi river confluences, East Coast of India. The TiO₂ content (av.51.49%) in ilmenite and rutile (94.47%), based on chemical properties, chlorate process is better than sulphate process in the extraction of TiO₂ from ilmenite in view of environmental protection. Almandine –Pyrope (Al-Py), garnets are of high concentration in coarse and medium fractions. In the monazites the \sum REE ranges from 43.47 to 67.78% (av.54.69%), \sum LREE varies from 42.90 to 64.08% (av.53.31%) and \sum HREE ranges from 0.57 to 3.70% (av.1.38%) in the study area. Monazites are suitable for extraction of LREE and Th, better understanding of the mineralogy, geochemistry, industrial suitability and radiological significances for the coastal placer deposits. The chemical grade of these heavy minerals is of high quality and contains less impurities and within the limits of industrial specifications. These heavy minerals of the present study area, Bhimunipatnam - Konada (BK), are of inferior quality when compared to those of Australia, China and U.S.A, and Q, MK, TN (India) and are superior to the OR Grade. This paper deals with industrial suitability of recent coastal sands of Gosthani and Champavathi river confluences.

Keywords: Ilmenite, Rutile, Garnet, Monazite, Gosthani River and Champavathi River

I. INTRODUCTION

As a result of liberalization and globalization, the inflow of private investments, especially in iron, steel, electronic and ceramics, magnets, catalysts, metallurgical alloys, phosphorus, water treatment, pigments and fertilizers industries, has increased, and some of the major user industries have gone in for expansion of their capacities to meet the increasing demand for their products. The increase in production in these sectors demands an enhanced supply of basic raw materials like Fe, Mn, Zn, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y oxides of various specifications. The coastal sands of the present study area (Bhimunipatnam- Konada) contains a group of seven economic heavy minerals viz. ilmenite, leucosene (brown ilmenite), rutile, zircon, sillimanite, garnet (almandine) and monazite. The heavies, distribution and concentration of these minerals and chemical

characterization of ilmenite, rutile, garnet and monazite were presented in terms of their chemical composition.

Many researchers [1-21] were reported heavy mineral occurrence and distribution from coastal sands in the study area and in other parts of Andhra Pradesh coast and Orissa coast.

In the present study deals with industrial suitability of the economic heavy minerals of recent coastal sands of Gosthani and Champavathi river confluences, the processing technology of beneficiation and metallurgical methods for metallic minerals is discussed.

1.1 Study Area

The 20km coastal stretch of the study area (83°26' to 83°36' E longitudes and 17°52' to 18°02' N latitudes) extends from the Gosthani River in the south to the Champavathi River in the north. These ephemeral rivers

originate in the Eastern Ghat hill ranges and constitute the drainage system. These rivers carry huge amount of sediment and debouch into the Bay of Bengal at Bhimunipatnam and Konada in the study area. The study area has different geological and geomorphic features generated by the rivers, small creeks and dynamic seasonal winds. In the study area average width of coastal sand deposit is 980m and dunes with maximum thickness of 18m. The location map of the study area is given in Figure 1.

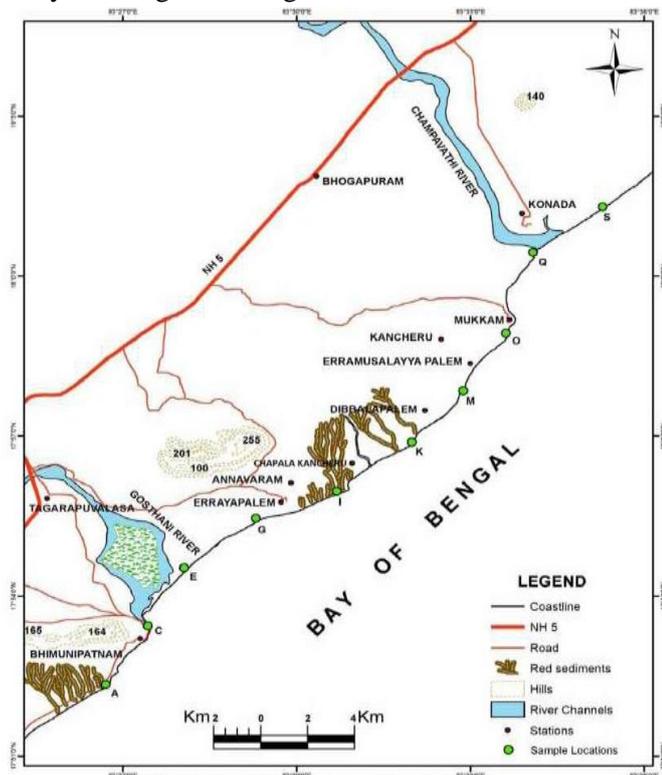


Figure 1. Sample location map of the study area

II. MATERIALS AND METHODS

2.1 Heavy Mineral separation

A total of thirty two representative samples were processed for heavy mineral studies. At each location, sediment sample was collected using PVC pipe of 3 inch diameter and 30 cm in length penetrated into the sediment layers to a depth of 10 cm. The representative 100 gm of properly dried sample is taken and soaked in distilled water to dissolve the salts and added 6% hydrogen peroxide, left over night. Repeatedly samples were washed to remove slime and dried. The slime free samples were treated with 10% dilute hydrochloric acid to remove carbonate material and washed. The dried samples were fractionized as +60, -60 to +120 and -120 to +230. These fractions were washed with SnCl₂ to remove iron oxide coatings on the grains

The three fractions of each sample i.e. +60 (Coarse fraction), -60 to +120 (Medium fraction) and -120 to +230 (Fine fraction) were taken for heavy mineral separation using Bromform (CHBr₃) (Sp. Gravity 2.89 g/cm³) as heavy medium. In each fraction magnetite portion of heavy minerals were separated with a horse shoe magnet, the magnetite free (non-magnetic) heavy mineral fractions were mounted on glass slides using Canada balsam as adhesive. By using petrological microscope attached with mechanical stage 300 – 350 grains were identified and counted on each slide following the line method [22]. The number percentages were calculated and converted into weight percentages [23].

Different sizes of sieves are used to make the samples into three (+60, +120 and +230) fractions. The data sets reveal that the heavy minerals are associated with medium (+120) fractions and only three minerals viz., opaques, sillimanite and garnet are more than 75% and other minerals i.e. rutile, zircon and monazite constitute 25%. The weight percentage of total heavy minerals varies from 12.37 to 24.32% (av.19.19%) in the northern and varies from 13.01 to 35.25% (23.19%) in the southern sector of the study area. The individual heavy mineral concentration variations show an increasing trend from north to south sector [21].

2.2 EPMA analysis

2.2.1 Grain Picking

Heavy mineral grains viz. ilmenite, rutile, garnet and monazite were identified under binocular petrological microscope based on their optical properties and picked for geochemical analysis by using Electron Micro Probe Analyzer (EPMA). Forty seven ilmenite grains, forty three rutile grains, sixty three garnet grains and fifteen monazite grains from two sectors of coastal sands between Bhimunipatnam and Konada.

2.2.2 Sample Preparation

Selected individual heavy mineral grains in each sample were mounted onto a standard size glass slide with resin (epoxy) for further lapping and polishing. This method allows imaging to be achieved using both transmitted and reflected light microscopy. Removal of excess sample and grinding to ensure the top and base of the resin blocks are parallel. Lapping was carried out to produce a smooth surface by using fine (600 grade) abrasive usually silicon carbide. Samples were polished with fine SiC-paper and a slurry of very fine alumina

ranging in size from 6 to 0.30 microns. The polished sample is then washed with clean water in an ultrasonic cleaner to get rid of the polishing grit and other surface dirt. The sample is then dried in air and cleaned with blow-duster.

For precise Wavelength Dispersive Spectroscopy (WDS) analysis, however, careful sample preparation is essential. Ilmenite, rutile, garnet and monazite are mounted in a non-conductive material and subjected to carbon-coating to dissipate excess charge produced by electrons beam. Furthermore, the standards and the sample should be coated to the same thickness. Carbon coating is carried out by carbon evaporation under vacuum. A polished glass block is used to monitor the thickness of carbon coat deposited on the specimens.

CAMECA SX-100 Electron Probe Micro Analyzer (EPMA), in Geological Survey of India, Hyderabad, used for geochemical analysis of ilmenite, rutile, garnet and monazite samples.

Polished surfaces of ilmenite, rutile and garnet samples are excited with an electron beam of accelerating voltage was kept at 15 keV and the beam current 20 nA. The beam size was kept at 1 μ m. Natural mineral standards were used for most elements (Orthoclase-Si and K; Corundum-Al; Wollastonite-Ca; Hematite-Fe; Chromite-Cr; Albite – Na and Al; Diopside- Mg and Ca ; Apatite- P ; Rhodonite- Mn; TiO₂ –Ti ; Almandine- Fe ; Nb on Nb and Ta on Ta). Polished monazite grains of coastal sands (15) in thin sections were selected for U–Th–Pb chemical dating, using a CAMECA SX-100 (EPMA). The operating conditions for analyses were 20keV of high voltage and 200nA beam current with the minimum possible beam diameter and it is assumed that the characteristic X-rays were generated from a volume represented on surface by an area of 2 μ m. Higher beam current was used for grains containing low thorium in order to have better statistics and lower errors. Calibrations were carried out at 20 keV and 200nA while analysis was obtained at higher beam current (200-400nA). PbM α was measured on LPET and the peak counting time was 300s with background measured on both sides. For uranium, the UM β line was used in order to avoid the interference of the ThM β line with a peak counting time of 200 s. U and Th were measured on PET crystal. Thorium M α peak was also counted for 200 s. Rare-earth elements and the X-ray lines measured included La (L α), Ce (L α), Nd (L α),

Pr(L β), Sm(L α), Ho (L β), Dy (L α) and Gd (L β) on spectral analysis considerations arrived at using virtual EDS. Counting time at peak varied between 50 to 85 s for these elements. Y L α line was used for yttrium and it was counted for 50s on peak. Interference of YL α on PbM α and ThM α on PbM α was corrected after measuring the interfering lines during calibration and thereafter applying the overlap correction. Other experimental conditions adopted in this work are similar to those in [24-26].

III. RESULTS AND DISCUSSION

3.1 Ilmenite

Ilmenite, leucoxene and rutile are titanium oxide minerals, serving as an important source for titanium metal and high quality of titanium dioxide pigment. Synthetic rutile and titanium slag are the products of ilmenite and are the source of titanium dioxide (TiO₂) pigment. That is insignificant compared to other countries with similar resources. Titanium is the 9th most abundant element in the earth crust. The important of titanium bearing minerals are ilmenite, leucoxene (altered product of ilmenite) and rutile, among which ilmenite is the chief source mineral for titanium. Ilmenite is smelted in electro-furnace direct for making ferrow – titanium alloys, titanium carbide is quite and hard material and can be used for cutting tools. Ferrow-carbon- titanium is alloyed with steel for high speed tools. It is also alloyed with chrome-steel.

Titanium oxide, called titanium white, is used for importing an ivory tint to artificial teeth, and as yellow glaze in pottery manufacture. It has opacity, twice that of zinc-oxide and three times that of lead-oxide this can be mixed with other pigments, without decreasing its opacity thus, titanium paints are pure titanium oxide or combined with other paint compounds. These are used in toilet articles, linoleum, artificial silk, white inks, colored glass and for dyeing leather and cloth, in the manufacture of electrodes and synthetic rutile. In the form of chloride titanium is used for removing colors from cloths, and in the form of tetrachloride for making smoke screens and sky writing.

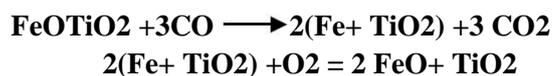
Very few geochemical studies have been carried out for ilmenite placer deposits of India in general and Bhimunipatnam- Konada (present study area) coastal placer deposit in particular.

The end member compositions of Fe-Ti oxides in northern sector of Bhimunipatnam –Konada coastal sands indicates that the ilmenite component varies from 69.92 to 99.89%, hematite varies from 0.00 to 25.45%, geikielite varies from 0.02 to 10.06% and pyrophanite varies from 0.02 to 1.40% (Table 3.1) and in southern sector the ilmenite component varies from 79.82 to 95.78%, hematite varies from 2.33 to 14.48%, geikielite varies from 0.02 to 5.53% and pyrophanite varies from 0.04 to 2.27%.

Titanium the metal of tomorrow end also known as “light weight champion” among the metals, finds a wide range of applications. Because of its high strength to weight ratio and resistance to corrosion, titanium is an important strategic and critical [27]. Because of its lightness, high strength and durability has been used in aerospace, aviation, chemical and electrical industries and manufacturing of surgical equipment. Titanium dioxide (TiO₂), a white pigment, because of its superior properties of high refractory index, low specific gravity, high hiding power, opacity and non-toxicity, is used in paints, plastics, welding rod coating, ceramics, chemicals, paper, rubber, fabric textiles, cosmetics and pharmaceuticals. Geochemical characterization is the most important character of TiO₂ pigment, a feedstock for adoption of suitable method in the processing for extraction of TiO₂ and implementation of waste disposal technologies.

For the manufacture of titanium dioxide pigment, ilmenite is first treated chemically to obtain upgraded ilmenite, which is commonly called synthetic rutile. There are two major processes of pigment production viz.

- a. Chlorate process in which the ore is chlorinated at 850° to 950°C in the presence of coke from which titanium tetrachloride (TiCl₄) is produced. This is oxidized in air at a raised temperature to produce TiO₂. Residual Cl₂ and HCl are removed by calcinations as follows:



- b. Sulphate process in which ilmenite (FeTiO₃) is dissolved in sulphuric acid. This process is as follows:



In which titanium sulphate is hydrolyzed to hydrated titanium dioxide and iron sulphate is removed as solid copper along with un-dissolved solids [28]. About three tons of sulphuric acid is used per ton of ilmenite. This process is not preferable as it involves many environmental problems due to different operating conditions and feedstock. Plants using chlorate process consumes high TiO₂ content feedstock like synthetic rutile and chlorate slag. On the other hand, plants adopting the sulphate process use low grade ilmenite and sulphate slag.

The chemical quality of ilmenite from major beach placer deposits of the world (U.S.A, Australia, Malaysia, South Africa, and India [Chavara (Q)-Kerala, Manavalakurichi(MK)-Tamil Nadu(TN), Chhatrapur-Orissa(OR) and Andhra Pradesh -Visakhapatnam, Kakinada and Srikakulam] are given in Table.1[29-30]. The chemical quality of ilmenite of the study area i.e. Bhimunipatnam - Konada (BK) in Andhra Pradesh is compared to the other deposits.

The ilmenites from U.S.A, Australia and Malaysia are of superior grade in terms of TiO₂ and the Indian ilmenites of Chavara (Q grade) is richest in its TiO₂ content (60%) and Manavalakurichi (MK grade) - 55% of TiO₂. The TiO₂ content (av.51.49 %) in the present study area, Bhimunipatnam - Konada (BK), is of inferior quality when compared to that of U.S.A, Australia and India (Q, MK, TN) and it is superior to the OR Grade.

Table 1.Quality of Ilmenite of Various Deposits in the World

Oxides (wt %)	USA	Australia		Norway- Rock	Malays ia	South Africa	India					Present Study area
	Florid a	Australi a1	Australi a2				Q	MK	OR	TN	AP	BK (AP)
TiO2	63.5	54-56	61	43.8	52	49.5	60	55	50.2	51-54	48-52	51.49
Fe2O3	27-31	18-24	32.5	12.7	6.5	25	25.5	18.9	12.8	11.0- 16.0	7.0- 17.4	45.67
FeO	4.7	16-22	3.6	34.3	34.3	22.5	9.7	20.9	34.1	28-33	30.9- 37.0	
Al2O3	0.73- 1.38	0.5-1.0	1.2	1.2	1.3	0.7	1.1	0.8	0.6	0.5- 0.55	0.30- 0.77	0.13
SiO2	0.06- 0.79	0.4-0.7	0.85	1.9	0.7	0.6	0.9	0.9	0.8	0.44- 0.90	0.40- 0.45	0.16
ZrO2	0.04- 0.19	0.05-0.15	0.25	0.01	0.13	NA	0.4	0.06	0.01	N A	N A
MnO	0.86- 1.63	1.4-1.7	1.06	0.33	26	1.2	0.4	0.4	0.55	0.3- 0.37	0.38- 1.14	0.38
Cr2O3	0.1- 0.12	0.03-0.04	0.11	0.02	0.02	0.2	0.13	0.08	0.05	0.04- 0.06	0.04- 0.07	0.08
V2O5	0.13- 0.16	0.12-0.22	0.18	0.2	0.04	0.3	0.15	0.22	0.24	0.21- 0.25	0.20- 0.22
MgO	0.17- 0.31	0.01-0.10	0.23	3.2	0.13	0.6	0.6	1	0.6	0.6- 0.67	0.48- 0.82	0.62
CaO	0.04- 0.15	0.01-0.10	0.02	0.5	0.13	0.1	0.2	0.2	0.2	0.02- 0.03	0.04- 0.13	0.03
P2O5	0.12- 0.18	0.02-0.04	0.14	0.04	0.1	NA	0.2	0.12	0.03	0.02	0.02- 0.57	0.05
U+Th (ppm)	69-162	40-140	160	<2	NA	<20	150	225	50-60	39-78	NA	NA

Q-Chavara, MK-Manavalakurichi, OR-Orissa, TN-Tamil Nadu, AP-Andhra Pradesh, and BK-Bhimunipatnam-Konada

Industrial specifications: Industrial specifications of ilmenite are TiO₂>50%; SiO₂<1.5%, Al₂O₃<1.0%;MnO₂<1.0%, Cr₂O₃<0.1%, P₂O₅<0.05% (sulphate route), P₂O₅<0.1%, CaO<0.2%, MgO<1.0% (chlorate route),

U+Th<1000ppm, preferred <500ppm, size of ore 100 microns >50% and 40 microns >90%. Ilmenitespecifications for the sulphate and chlorate processes for extraction of TiO₂ are given in Table.2. Sulphate method is not considered in these days

because, during initial heating, it emits gaseous hydrogen sulphide and sulphur dioxide which causes air pollution. Hence, chlorate process is better than sulphate process in the extraction of TiO₂ from ilmenite in view of environmental protection. In the

present study area, based on chemical properties, ilmenite is suitable for chlorate process and U+Th content is to be examined, because it has not been determined in the present study.

Table 2. Ilmenite industrial specifications

Oxides (wt %)	Sulphate route	Chlorate route	Present study area (BK)
TiO ₂	>50%	---	51.49
SiO ₂	<1.5%	---	0.16
Al ₂ O ₃	<1.0%	---	0.13
MnO	<1.0%	---	0.38
MgO	--	<1.0%	0.62
CaO	--	<0.2%	0.03
Cr ₂ O ₃	<0.1%	---	0.08
P ₂ O ₅	<0.05%	<0.1%	0.05
U+ Th	<1000ppm	<1000ppm	---

Source: Indian Rare Earths Limited (IREL)- A Govt of India undertaking – Department of Atomic Energy

3.2 Rutile

The chemical quality of rutile from all over the world - U.S.A, Australia, Malaysia, South Africa, and India [Chavara(Q)-Kerala, Manavalakurichi(MK)-Tamil Nadu(TN), Ganjam and Chatrapur-Orissa(OR) and

Andhra Pradesh (BK)] are given in Table.3. The chemical quality of rutile of the study area i.e. Bhimunipatnam- Konada (BK) in Andhra Pradesh is compared to that of the deposit of rutile from other countries.

Table 3. Rutile and Garnet grades in India

Rutile				
Oxides (wt %)	MK Grade	OR Grade	Q Grade	BK Grade(study area)
TiO ₂	94.4	94.5	95.05	94.47
Fe ₂ O ₃	1.9	1.1	0.7	0.23
SiO ₂	1.8	0.9	1	0.06
P ₂ O ₅	0.05	0.08	0.05	0.03
ZrO ₂	1.8	0.9	1.4
U	66ppm	Trace	Trace
Th	94ppm	NA	NA
Garnet				
Oxides (wt %)	MK Grade	OR Grade	AP Grade (BK) study area	
SiO ₂	40	36.3	37.85	
TiO ₂	1	1.3	0.04	
Al ₂ O ₃	21	19.8	21.16	
Fe ₂ O ₃	2.9	3.5	1.07	
FeO	26	27.9	27.45	
MnO	0.5	0.59	
MgO	6.8	6.8	7.55	
CaO	0.9	2.8	2.05	
P ₂ O ₅	0.03	

Source: Indian Rare Earths Limited (IREL)-A Govt of India undertaking – Department of Atomic Energy

Industrial specifications: In India, [32] is a Government undertaking company and has three heavy mineral separation plants i.e (a) Manavalakurichi (Tamil Nadu), (b) Chevvara (Kerala) and (c) Gopalpur (Orissa) for extraction of rutile and other heavy minerals. The minimum TiO₂ content required for separation from rutile in the above plants is 94% TiO₂ (min) for MK, 95% TiO₂ (min) for Chavara and 94.25% TiO₂ (min) for Gopalpur. The other private extraction plants viz., Kerala Minerals & Metals Ltd., Chavara and V.V. Mineral Distt. Thoothukudi (Tamil Nadu) are using rutiles with TiO₂ content of 93.20% and 95% respectively.

The rutiles from Australia, South Africa, Sierra Leone, Ukraine are of superior grade in terms of TiO₂ and the Indian rutiles from Chavara (Q grade) is richest in its TiO₂ content (95.05%) and Manavalakurichi (MK grade)-94.4% of TiO₂. The rutiles from the present study area, Bhimunipatnam - Konada (BK) are of inferior quality when compared to those of U.S.A, Australia (world) and Q, MK, TN (India) and similar to the OR Grade.

3.3 Garnet

Garnets are nesosilicates and are crystallized in cubic system with general formula X₃Y₂Si₃O₁₂. The most common end member species are almandine (Fe₃Al₂Si₃O₁₂), pyrope (Mg₃Al₂Si₃O₁₂), spessartine (Mn₃Al₂Si₃O₁₂), grossular (Ca₃Al₂Si₃O₁₂), andradite (Ca₃(Fe,Ti)₂Si₃O₁₂) and uvarovite (Ca₃Cr₂Si₃O₁₂). The almandine variety has great economic value in the world market because of its various applications.

In the study area, garnets are predominantly 80% of analyzed samples are solid solution of almandine – pyrope (Al-Py), remaining 20% of analyzed samples are solid solution of almandine-pyrope- grossular (Al-Py-Gr) and spessartite is low content.

Garnets are used for manufacture of blasting media, abrasives, grinding wheels, mosaic cutting stones, decorative wall plasters, ceramics, polishing of picture tubes, glass polishing and antiskid surface for roads, air strips, runways, water filter, water jet cutting, artificial granite tiles/heavy duty floor tiles, cleaning of casings/pipes in petroleum industry and as a gemstone.

The present study results well corroborate with electron probe micro analyzer (EPMA) studies of garnets from

different litho units viz., charnockites and khondalites from central Eastern Ghat Mobile Belt of India [33]; garnets from beach placers of Srikurmam area [34] and garnets from southern India [35]. The Cr₂O₃, CaO and MgO and molecular proportions indicates that garnets were derived from khondalites, leptynites and charnockites.

Garnet is a dark reddish brown mineral with sharp angular fractures and has high resistance to physical and chemical corrosion. Garnets, on fracturing, continuously exhibit set of fresh sharp edges. Garnets are highly used as abrasives. Low quality garnets are used in sand blasting in removing corrosive cover of air craft, vehicles and ships and substitute silica sand because of its high specific gravity of 3.5 to 4.2. Garnets require only 60% of the air pressure when compared to silica sand. It is used in water filtration as it resists physical and chemical break down during the process. Some varieties of garnets are used as gemstones. The quality of garnets is expressed mostly by their physical characteristics such as inertness, angularity, hardness and specific gravity rather than its chemical purity. Garnets of detrital origin have rounded shape and therefore they have applications' in sand blasting and water jetting.

Garnets of the study area are of high (>99%) concentration in coarse and medium fractions i.e. +60 and -60 to +120 ASTM sieve sizes and of the -120 to +230, concentration in less than 2% (wt %).

Geochemical studies of garnets reveal that, sediments contain almandine (also known as almandite), a common abrasive garnet, highly suited for abrasive blasting because of its hardness (7.0-8.5 Moh's Scale), less brittleness and its capability to retain individual crystalline forms even in fine mesh sizes. It has an impact of 2-3 times greater than that of silica sand of the same grain size. About 50% of the material can be recovered and recycled 2 to 3 times and hence, more expensive. Almandine garnet does not contain any free silica. There is no leaching of heavy metals during industrial applications and hence, is eco-friendly as it does not produce any health hazards and has price advantages when compared to the silica and copper slags.

Industrial specifications: Industrial specifications of garnets SiO₂= 37%, Al₂O₃= 25%, Fe₂O₃=

33%, MnO=1%, CaO =1% and MgO=3%. Garnets of Bhimunipatnam - Konada coast are of under prescribed specifications. Major elemental concentrations of garnets of northern sector contains SiO₂=37.89%, TiO₂=0.03%, Al₂O₃=21.10%, FeO=30.17%, MnO=0.69%, MgO=8.15%, CaO=1.69%, Na₂O=0.02%, K₂O=0.02% and Cr₂O₃=0.03%. In the southern sector, garnet contains SiO₂=37.83%, TiO₂=0.04%, Al₂O₃=21.24%, FeO=30.67%, MnO=0.47%, MgO=6.89%, CaO=2.45%, Na₂O=0.03%, K₂O=0.01% and Cr₂O₃=0.54%.

The garnets from Australia, China and U.S.A, are superior grade in terms of SiO₂, TiO₂, Al₂O₃, Fe₂O₃, FeO, MnO, MgO, CaO and P₂O₅. The Indian garnets of Manavalakurichi (MK grade) and Orissa (OR grade) are given in the Table.3. Garnets of the present study area, Bhimunipatnam - Konada (BK), are of inferior quality when compared to those of Australia, China and U.S.A, and Q, OR (India) and are superior than the OR Grade.

3.4 Monazite

Monazite is the chief source of Thorium and Rare earth elements (REE) are a group of 17 metallic elements and it consists of 15 lanthanides (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) along with scandium and yttrium. These rare earth elements are divided into two groups i.e., lighter rare earth elements (LREE) – La to Sm and heavier rare earth elements (HREE) – Gd to Lu. LREE + Sc is called as cerium group and HREE + Y is called as yttrium group. ThO₂ and REE contents are most important for extraction of monazite.

The average LREE concentration is 53.31% which is more than HREE (av.1.38%). High ratios of \sum LREE/Y and \sum LREE more than actinides (Th +U) indicate that provenance for monazite in the study area is garnet bearing paragenesis rocks such as metapelitic rocks (khondalites, pyroxene granulites) and charnockites.

Monazite is a reddish-brown phosphate mineral containing rare earth metals. It occurs usually in small isolated crystals. Monazite is an important ore for thorium, lanthanum, and cerium. It has a hardness of 5.0 to 5.5 and is relatively dense, about 4.6 to 5.7 g/cm³ and because of the presence of thorium, it is a radioactive mineral.

Monazite is an anhydrous thorium-bearing orthophosphate of the cerium earths. Monazite generally forms small grains, rarely larger than a few hundredths of an inch across. They occur as accessory minerals in plutonic rocks and natural mechanical concentration deposits (placers).

Thorium, as an unexploited energy resource, is about four times more abundant than uranium in the Earth's crust and serves as an important fuel resource. It occurs in association with the rare earth elements, yttrium and scandium, which acquire heightened interest in their use in critical new technologies.

The increased availability and decreasing extraction cost of the rare earths is expected to introduce them into new applications. They make Th readily available as a byproduct. Eventually, primary Th ores such as thorite and monazite could be accessed. The depleting hydrocarbons as well as the uranium resource bases mandate the consideration of alternative energy sources, including thorium-based cycles which are otherwise a valuable yet unused energy resource. The presence of radioactivity in the rare earth ores must be carefully dealt from the health point of view. Th and U can be extracted as byproducts from them.

In mining activities, Total Rare Earth Oxides (TREO) refers to the elements lanthanum to lutetium, plus yttrium are expressed as oxides. Heavy Rare Earth Oxides (HREO) refers to the elements Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y and expressed as oxides as a percentage of the TREO. Light Rare Earths (LREO) refers to the elements La, Ce, Pr, Nd, and Sm and expressed as oxides. Neodymium, Dysprosium, Terbium and Europium are in high demand.

The economics of rare earths extraction involves the balance between the "Heavies" and the "Lights." The rare earths occur together as a group and must be sequentially separated at additional effort and cost. Most deposits are tilted towards the LREOs which constitute 97-99 percent of the resource base. Deposits having an unusual balance with a high proportion of the HREOs > 20 % is rare, and consequently more valuable. For instance, light cerium can be purchased for about \$4 / kg, whereas heavy europium goes for \$470 / kg.

The refining process of each element is performed using solvent extraction or ion exchange processes. The

balance of chemicals used and the design of the processes depend on the composition of the feedstock concentrates. Solvent extraction is commonly used for the light elements, whereas the ion exchange process is used for the heavy ones.

Industrial Specifications: Chemically, Indian monazite sands contain 8-10 wt% ThO₂; 60-66 wt% REO; and 20-25 wt% P₂O₅ [1] as major constituents. The study of monazite sands provides a better understanding of the mineralogy, geochemistry, industrial suitability and radiological significances of the coastal placer deposits.

The chemical composition (wt %) of monazites of Bhimunipatnam – Konada coastal sand deposit is as follows. The ThO₂ content varies from 3.78 to 13.39% (av.9.42%), Y₂O₃ ranges from 0.00 to 2.26% (av.0.36%), SiO₂ varies from 0.48 to 2.85% (av.0.85%), CaO from 0.7 to 1.76% (av.1.29%), and UO₂ varies from 0.03 to 0.42% (av.0.13%). The \sum REE ranges from 43.47 to 67.78% (av.54.69%), \sum LREE varies from 42.90 to 64.08% (av.53.31%) and \sum HREE average is 1.38% and its varies from 0.57 to 3.70% (Table.4). Monazites are suitable for extraction of LREE and Th.

Table 4. Typical composition of monazites processed in Indian Rare Earths Limited (IREL)

		BK(Study Area)
Total oxides (wt %)	68%	66%
ThO ₂	9%	10.45%
RE ₂ O ₃	59%	54.89%
P ₂ O ₅	27%	29.29%
Insolubles	3%	3.58%
CaO	0.50%	1.31%
MgO	0.10%	---
Fe ₂ O ₃	0.20%	----
Al ₂ O ₃	0.10%	----
PbO	0.18%	0.36%
U ₃ O ₈	0.35%	0.12%

Source: Indian Rare Earths Limited (IREL)-A Govt of India undertaking – Department of Atomic Energy

The rare earths industry all over the world prefers to use the mixer settler as the contacting equipment. They are popular because of the simplicity of operations and design, low capital cost even though the solvent hold up inventory is high. Mixer settlers of MS-FRP construction having mixer capacity of 100 liters designed for maximum solvent throughput of 3000 liters per hour at maximum aqueous throughput of 3000 liters per hour are used.

He [36] was using solvent extraction process using PC-88AAS extractant to produce neodymium oxides, suitable for the manufacture of neodymium –iron-boron magnets, starting from monazite sands. The success of this process has re-established the effectiveness of this technique for the separation of rare earths. Solvent extraction has been fully accepted as the most useful separation process and will

continue to be the most sought after separation techniques in the rare earth industry for a long time to come.

IV. CONCLUSIONS

India can be happy about the bountiful reserves of ilmenite, rutile, garnet, and monazite with favorable factors like liberalized mineral policy of government, proximity to port etc. unless the resource are converted exploitable reserves fit for various industrial applications, our country will not benefit, a few issues like technology for up gradation.

- ✓ Ilmenite serve as an important source of titanium metal and in the manufacturing of synthetic rutile and rutile is used as a high grade pigment.

- ✓ The TiO₂ content (av.51.49 %) in the ilmenite of the present study area from Bhimunipatnam - Konada (BK) is of inferior quality when compared to U.S.A, Australia and Q, MK, TN (India) and it is superior than the grade of Chhatrapur of Orissa in India(av.50.2%).
- ✓ Chlorate process is better than sulphate process in extraction of TiO₂ from ilmenite in view of Environmental Protection.
- ✓ The present study area (Bhimunipatnam – Konada) the TiO₂ content in rutile (av.94.47%) are of inferior quality when compared to U.S.A, Australia (world) and Q, MK, TN (India) and are similar to the Chhatrapur grade of Orissa. (av.94.5%).
- ✓ Geochemical studies of garnets reveals that, coastal sediments in the study area which contains almandine (also known as almandite) are opted for sand blasting in abrasive industry and for water jet-cutting in the study area, because of its hardness and angular to subangular nature (less transported), rounded (more transported).
- ✓ Garnets in the study are more in medium fraction rather than coarse and fine fractions in the study area.
- ✓ The garnets of the study area are of inferior quality when compared to Chavara of Kerala, Manavalakurichi of Tamil Nadu (India) and superior to the grade of Chhatrapur of Orissa.
- ✓ The chemical grade of these heavy minerals is of high quality and contains less impurities and within the limits of industrial specifications.
- ✓ In the monazites the \sum REE ranges from 43.47 to 67.78% (av.54.69%), \sum LREE varies from 42.90 to 64.08%(av.53.31%) and \sum HREE average is 1.38% and it varies from 0.57 to 3.70% in the study area. Monazites are suitable for extraction of LREE and Th.
- ✓ The study of monazite sands provides a better understanding of the mineralogy, geochemistry, industrial suitability and radiological significances for the coastal placer deposits.
- ✓ The distribution and concentration of economic heavy minerals, the grain size distribution and geochemical characteristics of heavy minerals indicate that the coastal sediments of study area are economically suitable for heavy mineral extraction and their processing.

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