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A Study on Chemical and Mineralogical aspects of Placer Ilmenites from North Coastal Andhra Pradesh – with reference to its Industrial Suitability

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ABSTRACT:

Placer Ilmenites from the north coastal Andhra Pradesh, India Viz, Kalingapatnam, Srikurmam, Visakhapatnam-Bhimunipatnam deposits have been studied for their mineralogy and chemistry with their applicability to different industries. It was noticed that Ilmenites from these three deposits show more exsolutions at grain level like ilmeno-hematite, hematite-ilmenite, ilmenite-rutile. Some irregular exolved phases and needle like hematite within the ilmenite matrix and alteration of ilmenites is noticed. The influence of these exsolutions and intergrowth on industrial working has been analysed, with special emphasis on the impact of high iron content in the placer ilmenites in the form of hematite on the industrial working is brought out. When considering the chemistry, it was noticed that TiO_2 content is different in these deposits, Kalingapatnam (53.54% max), Srikurmam (51.95% max) and Visakhapatnam-Bhimunipatnam (48.18% max). While the Total Iron (Fe) content varies as in Kalingapatnam (46.81% max), Srikurmam (47.02% max) and Visakhapatnam-Bhimunipatnam (52.26% max), some trace elements were also noticed especially concentrations like V, Cr, Co and Mn etc., which are considered as noxious nature in preparation of desired product like synthetic rutile which is very important product in titanium metal production. The chemical data of these trace elements was used to make necessary steps to setup successful metallurgical process. Based on the data generated from mineralogical and chemical aspects it was observed the placer lmenites from these deposits are preferred for pigment manufacturing.

KEY WORDS: Placer Ilmenite, North Coast, Kalingapatnam, Srikurmam, Visakhapatnam-Bhimunipatnam, Mineralogy, Exsolutions, Chemistry, Toxic, Pigment.

INTRODUCTION:

Ilmenite is a common accessory mineral found mostly in igneous rocks. It is black iron titanium oxide with composition $FeTiO_3$. Mostly ilmenites are formed during slow cooling of magma chambers and are concentrated through process of magmatic segregation. As the magma cools down crystals of ilmenite form at particular temperature and these crystals are heavier than surrounding melt and sink to bottom of magma chamber. This results in the accumulation of ilmenite and similar minerals like magnetite are also present at the bottom of magma chamber. The ilmenite bearing rocks are often gabbro, norite or anorthosite. It also crystallizes in veins and cavities and sometimes occurs as well-formed crystals in pegmatite. Ilmenite has high resistance to weathering. When rocks containing ilmenite weather, grains of ilmenite disperse with sediment. Grains with high specific gravity segregate during stream, transport and accumulate as heavy mineral sands. These are mechanically

transported and concentrated in beaches, rivers, dunes and offshore environments. In India East and West Coast beaches are characterised by placer Ilmenites along with Garnet, Sillimanite, Rutile, Zircon and Monazite.

The Ilmenite isblack iron titanium having composition $FeTiO_3$. Ilmeniteis a primary ore of titanium metal, which is very essential in the present – day technology. Ilmenite occurs all over the world and it is majorly used in space technology, preparing arms and in manufacture of titanium dioxide. Ilmenites reserves are almost 2.5 billion tons as estimated, out of which India with its huge coastline comprising almost 625.57 million tons (IBM Reports, 2017).Placer Ilmenites which occur along the coast of Andhra Pradesh alone are almost 82 million tons (IBM Reports, 2017) which are of estimated reserves.

Table 1: Ilmenite Resources of Andhra Pradesh

Andhra Pradesh	In Million Tonnes
BhavanapaduHukumpet	10.18
Kakinada	13.84
Kalingapatnam	5.80
Narsapur	2.92
Nizampatnam	19.26
Srikurmam	8.60
Bhimunipatnam-Visakhapatnam	2.88
Amalapuram, Bapatla, Chirala	10.39
Vetapalem Coast	5.31
Total	**82.28**

Source: IBM Annual Report, 2017.

STUDY AREA:

The study is concentrated with the deposits of Bhimunipatnam – Visakhapatnam, Srikurmam and Kalingapatnam of North Coastal Andhra Pradesh (Figure 1). Few earlier works on mineralogical and chemical aspects were carried out on Srikurmam (JagannadhaRao, 2008 and Sandeep, 2019), Bhimunipatnam – Visakhapatnam (Sastry, 1987; Rao, 1983; Sandeep, 2019), and Kalingapatnam (JagannadhaRao, 2008). In this present study characterisation of these ilmenite deposits is made by mineralogical and chemical studies to establish their suitability for industries.

Figure 1: Study Area Map

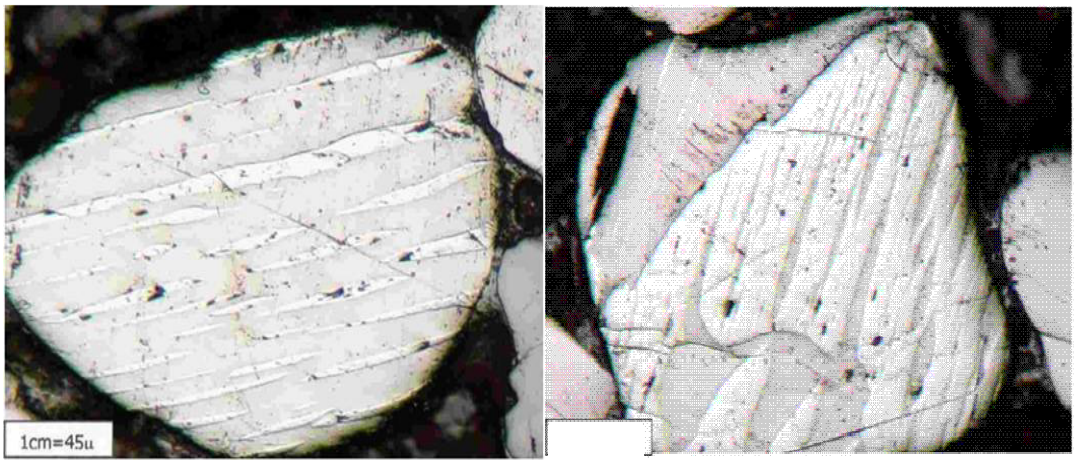
METHODOLOGY:

For the Mineralogical studies of Ilmenite, bulk sample collected was reduced to the required sizeby using standard reduction procedure. Heavy minerals were concentrated by bromoform and the magnetite in the sample was separated by hand magnet. The Magnetite free samples wererun through isodynamic separator for 3 or four times for each sample at 0.25 amp to separate pure ilmenite from the sample. These pure ilmenites were made into polished sections formed in araldite medium are studied under Lecia DMLP microscope for their Mineralogical aspects. These Pure Ilmenites that were separated through isodynamic process were analysed by atomic absorption spectrophotometer, Perkin Elmer make, model-AS200 and ICP-MS for major and trace elemental studies.

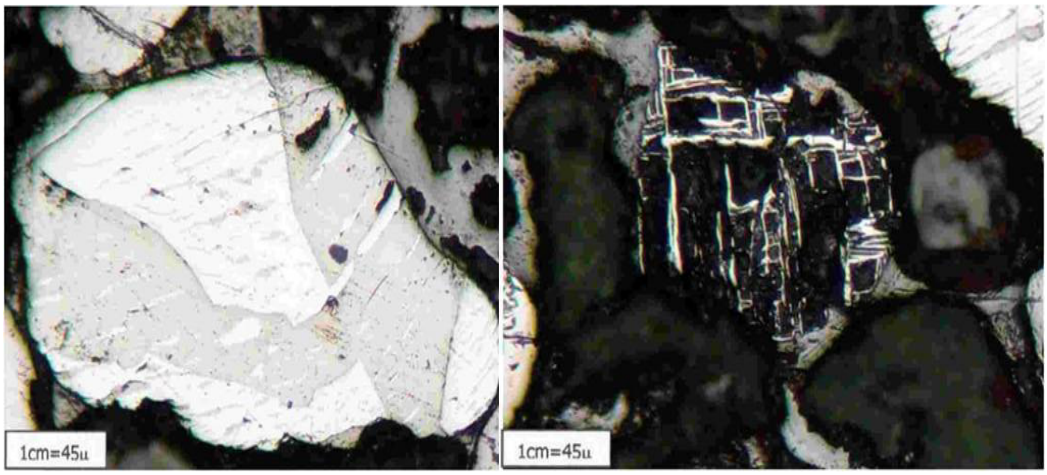
RESULTS:

MINERALOGY:

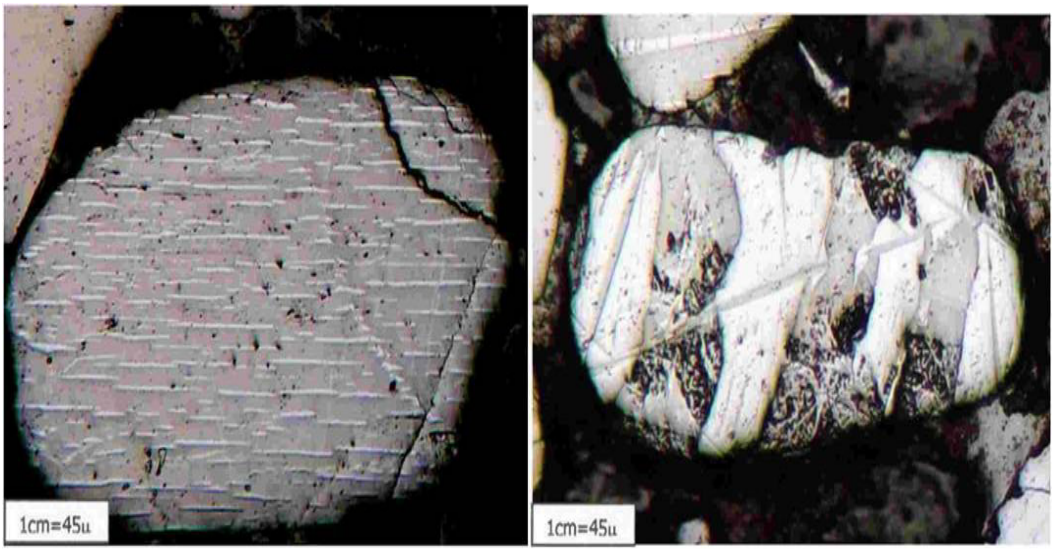
The ore microscopic observationsof the pure ilmenite grains from Kalingapatnam revealed that some grains are having exsolutions mainly as exolved phases of Ilemenite-rutile, Ilmenite-hematite, hematite-ilmenite (figure.2 – b). Also, many complex exolved phases are also observed, formation of lamellae features with dominant ilmenite is named as ilmeno-hematite, and hematite dominant is named as hemo-ilmenite, and some intergrowth lamellae of hematite and ilmenite phases are also observed. Ilmenites from Visakhapatnam-Bhimunipatnam deposit grains were perfectly rounded and some were irregular (JagannadhaRao, 2006; Sandeep, 2019). This Visakhapatnam-Bhimunipatnam deposit features of exsolutions of ilmenite-hemaite, hemo-ilmenite and when compared, these resemble to Cox Bazar (Sam Suddin, 1992) and some skeletal textures (figure.2 – d) are observed. Even the Srikurmam deposit contains exsolutions (figure.2 – a, b) with mineral phases of ilmenite-hematite, hematite-ilmenite and ilmenite-rutile, some needle like hematite within the ilmenite matrix mymekitiic texture (figure.2 - e) along with alteration of ilmenite (figure.2 - f) is also observed.



a. Simple exsolutions **b. Complex exsolutions**



c. Irregular Ilmenite and hematite exolved phases **d. Skeletal Texture**



e. Needle like hematite with in ilmenite matrix Mymermekitic texture **f. Alteration of ilmenite along grain boundaries**

Fig.2.- a, b, c, d, e, f: exolved phases of ilmenites from three deposits

CHEMISTRY:

Ilmenite samples from the study areas Kalingapatnam, Srikurmam and Visakhapatnam-Bhimunipatnam deposits were studied for their major radicals with weight percentages and trace elemental concentrations in parts per million (PPM) are shown in the Table-2.

The Chemical results indicate that TiO_2 varies 51.08%-53.54% in Kalingapatnam deposit, 46.12%-54.30% in Visakhapatnam-Bhimunipatnam deposit, and 50.04%-52.05% in Srikurmam deposit. Total Fe content 45.18%-46.81% in Kalingapatnam deposit, 44.10%-52.26% in Visakhapatnam-Bhimunipatnam deposit and earlier study by JagannadhaRao (1985) and Sandeep (2019) also reported high iron content in Bhimunipatnam, 45.41%-47.53% in Srikurmam deposit. The major radicals like SiO_2, Al_2O_3 and MgO are in lower average values as represented in the Table-2.

Table 2: Chemical Analysis of Ilmenites (Major radicals with wt.% and Trace Elements in ppm)

	Sample	TiO_2	SiO_2	Al_2O_3	Fe	MgO	Cr	Mn	V	Co	Ni	Zn	Cu
Kalingapatnam deposit	1	51.08	0.3	0.27	45.27	0.17	722	0.84	1212	294	58	422	75
	2	52.02	0.5	0.25	46.81	0.19	708	0.95	1236	302	60	480	71
	3	53.54	0.3	0.26	44.04	0.17	711	0.68	1222	320	56	521	63
	4	51.59	0.4	0.25	45.18	0.18	693	0.93	1301	306	59	533	68
	5	52.94	0.5	0.27	46.5	0.19	699	0.75	1198	311	57	498	61
	Avg	52.23	0.4	0.26	45.56	0.18	706.6	0.83	1233.8	306.6	58	490.4	67.6
Bhimunipatnam-Visakhapatnam.	1	47.36	0.24	0.41	49.95	0.4	1568	1.27	3338	590	86	495	66
	2	48.18	0.5	0.28	49.28	0.2	1289	0.31	3271	211	170	273	37
	3	53.5	0.8	0.3	44.34	0.32	1067	1.13	1526	236	96	686	75
	4	47.84	0.4	0.44	45.1	0.34	1208	0.63	2393	311	192	526	42
	5	46.12	0.18	0.52	52.26	0.26	1021	0.87	1335	245	121	613	56
	Avg	48.6	0.424	0.39	48.186	0.304	1230.6	0.842	2372.6	318.6	133	518.6	55.2
Srikurmam deposit.	1	51.12	0.38	0.17	46.66	0.2	651	0.74	1302	319	46	697	67
	2	52.05	0.37	0.16	45.84	0.3	653	0.52	1304	320	49	694	65
	3	50.65	0.39	0.18	47.53	0.2	618	0.93	1303	316	45	698	68
	4	50.04	0.38	0.18	45.41	0.4	651	0.69	1300	320	45	695	65
	5	51.95	0.37	0.17	47.02	0.3	649	0.81	1300	315	47	696	68
	Avg	51.16	0.37	0.17	46.49	0.28	650	0.73	1301.8	318	46.4	696.4	66.6

In the Chemical study of trace elements Mn, V, Co, Ni Zn, Cu and Cr are also determined. In these trace elemental concentrations of Vanadium recorded 3338 ppm in Visakhapatnam-Bhimunipatnam, 1236 ppm in Kalingapatnam and 1304 ppm in Srikurmam deposit. Earlier study by JagannadhaRao (2008) also reported high amount of Zinc in Srikurmam placer deposit and Sandeep (2019) also reported. In the chemical study Zinc concentration varies in all deposits and high concentration of Zn

was reported from Srikurmam deposit with 698 ppm. WiletheCr values of Bhimunipatnam are almost 1568 ppm, 722 ppm in Kalingapatnam deposit, 653 in Srikurmam deposit.Co, Mnand Ni concentration are also determined in the Table-2.

DISCUSSIONS:

Titanium metal which is one of the toughest metal which has the capability to withstand high temperature and pressure reactions from acids or gases, and also corrosion resistance and light weight.Inthe world 95% of titanium production is consumed in the form of titanium dioxide as a pigment used in paints, plastics. The titanium dioxide paints will possess the property of great reflectors of infrared radiation and highly used by astronomers. Different alloys of titanium are used as cover metal for aircrafts, combat armours, naval ships, missiles and space crafts and in nano technology. Titanium is alloyed with different metals such as iron, manganese, molybdenum mostly and partially with other metals. The study areas describe variations in the Titanium dioxide, and variations in major radicals as shown in the Table-2.

Titanium which is obtained from the Ilmenites is by purification. The Placer ilmenites obtained from the study areas having 50% (maximum) of titanium content, as it is processed to synthetic rutile or slag by two different processes namely: Chloride Process or Sulphate process (Manuel, 2014). Placer Ilmenites are improved to have 70%-90% content of TiO_2 bythe process of electro-smelting and next for further purification to maximum titanium dioxide content chloride or sulphateprocesses are initiated depending upon the purity of titanium dioxide and usage of industry.

Because of the presence of exsolutionsin these ilmenites which will lower the quality of ore and quantity of ore recovery, exsolutions between the exolved phases of ilmeno-hematite, hemo-ilmenite, ilmenite-rutile and intergrowths which considerably increased the quantity of iron in the ilmenite which eventually decreases the quality of ilmenite as well as the quantity of ore reserves.Kalingapatnam,Visakhapatnam-Bhimunipatnam, and Srikurmam deposits have extensive exsolutions with exloved phases and intergrowths. TiO_2 of the present study areas revealed that from Kalingapatnam and Srikurmamshows alittle highTiO_2Content more and low iron content when compared to Visakhapatnam-Bhimunipatnam. As in all deposits Ilmeniterecorded less TiO_2andhigh iron content (than the theoretical formula of the Ilmenite. {Deer, 1965}). Earlier work carried out on mineralogy (JagannadhaRao, 2006; Raju, 2018; JagannadhaRao, 2018; Sandeep, 2019) also reported extensive exsolutions withexolvedphases in the Bhimunipatnam-Visakhapatnam and Srikurmam deposits.

As the geochemical data (Table-2) suggest that the placerilmenite deposits of the present study area are atmostsuitable in manufacturing of TiO_2 pigment. The three deposits contain TiO_2 around (47%-53%), iron content (43%-52%), which the presence of exsolutions gave high iron content to the placer ilmenites are considered as polluting agent and which it can consume more amount variable chemicals in manufacturing of TiO_2 or $TiCl_4$by fixed process (Manuel, 2014).Chloride process is most applicable for these deposits and it is also the most preferred method. Asthe reason being that it hasgood efficiency and also environmentally safe for preparing the product synthetic rutile (Bencher and Benilite process) or slag(Manuel, 2014). The presenceof trace elements in different amounts like Ca, P, V, Co etc.,can affectthe properties of pigment being preparedand are regarded as toxic

elements (Manuel, 2014) which will have negative impacts in the preparation of the desired product (Akbar 2012).

The trace elements like Ca, Cu, and Nireported as normal inthethreeeedeposits. In Visakhapatnam-Bhimunipatnam, Srikurmam and Kalingapatnam trace elements V, Ni vary around 3300 ppm, 86 ppm (maximum), 1300 ppm, 45 ppm (maximum) and 1236 ppm, 60 ppm (maximum) respectively. Visakhapatnam-Bhimunipatnamdepositconsists ofhigher amount of trace elements which will eventually affect the properties of the product grade of the pigment and also will have very low economic importance, the other two deposits KalingapatnamandSrikurmamhave an average amounts of trace elemental concentrations which will not affect the pigment grade and processing of the Ilmenite.

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