CHAPTER 2

ILMENITE RESEARCH- A REVIEW

Although research on ilmenite started only at the turn of the century, it has now emerged as an important topic of discussion among scientists due to its relevance as the common ore of titanium, the metal of the 21st century. Of particular interest to mineralogists and metallurgists is the alteration of ilmenite, since the TiO$_2$ content is progressively enriched along with the change in iron ions and trace elements.

2.1 TRENDS OF RESEARCH ON ILMENITE

A pioneering attempt in this direction was made when Palmer (1909) termed the alteration product arizonite, which is high in ferric content. Later Creitz & Mcvay (1949) and Spencer (1948) suggested that occurrences of leucoxene might be actually a product of the weathering of ilmenite. Cannon (1949) correlated the variation of titania content with the degree of alteration of the mineral. Gillson (1950) stated that arizonite is not a weathered product of ilmenite, questioning the view proposed by Overholt et al (1950). Later on it was established that alteration is accompanied by removal of ferrous ions from the mineral structure (Lynd et al, 1954) and the crystal lattice undergoes progressive break down (Bailey and Cameron, 1957).

Further, the composition of the alteration product of ilmenite has been attempted by many workers. According to Flinter (1959), ilmenite undergoes alteration to form a mixture of ilmenite and 'diffuse' rutile. Kharkanavala and Momin (1959), from studies on Chavara leucoxene concluded that it contained rutile, pseudo brookite, anatase and haematite; while Buddington & Lindsley (1964) suggested a mixture of
haematite, rutile, anatase and ilmenite. Temple (1966) & Teufer and Temple (1966) described the alteration product of ilmenite as pseudorutile, since it has a pseudo hexagonal structure and similar properties of rutile and described its chemical composition. Dyadchenko & Khatutseva (1960) assigned a variable composition for this mineral. Gevorkyan and Tanavayev (1964) described this alteration phase as a mixture of titanium and iron oxides, while Grey et al (1983) specified pseudorutile as a mixture of goethite rutile intergrowths. Haggerty (1976) and Rumble (1976) are of the view that ilmenite alters essentially to rutile and haematite. The geochemical significance of ferrous to ferric conversion during alteration has been studied in detail (Shirane et al, 1962; Ronov & Taroshovsky, 1971; Carranza & Cox, 1979; White, 1990).

Bailey et al (1956) first formulated the delineation and identification of the stages of alteration of ilmenite on the basis of microscopic observations and X-ray studies. By progressive alteration, ilmenite evolves into 1) patchy ilmenite 2) amorphous Fe-Ti oxides and ultimately 3) leucoxene. Braksdale (1966) argued that rutile is the final end product of ilmenite alteration before passing through an amorphous stage. Grey & Reid (1975) and Dimanche & Barholme (1976) explained the alteration of ilmenite as a two-stage mechanism in which ilmenite forms pseudorutile in groundwater environment, followed by a process of rutile formation by a dissolution precipitation process (Grey & Reid, 1975; Pakharykov et al, 1979; Frost et al, 1983). The question of alteration of ilmenite to rutile being a continuous process or not has had been hotly debated (Chaudhuri et al, 1988,1989). Mucke and Chaudhuri (1991) is of the opinion that it is a continuous process and they have named yet another alteration phase between ilmenite and pseudorutile. However, Chaudhuri & Newsley (1990) and Hugo & Cornell (1991) opined that the end product of leucoxene can form directly from ilmenite, without the formation of intermediate phases. The terminology for the various stages of alteration
as proposed by Frost et al (1983), namely, ferric ilmenite, hydrated ilmenite, pseudorutile and leucoxene is now commonly accepted.

The important changes in physical properties during weathering include considerable variation in magnetic susceptibility and density (Bailey et al, 1956; Flinter, 1959 and Braksdale, 1966). Comprehensive studies in this direction were further taken up by Hoffman (1975) and Wort and Jones (1980). Frost et al (1986), Garanin et al (1989) and Braksdale (1966) studied the porous nature of altered crystals and its effect on density.

An increasing application of chemical studies of ilmenite, is for the delineation of provenance and age of sediments. Though Hutton (1950) & Buddington & Lindsley (1964) had mentioned the compositional variation of the mineral, according to heterogeneity of source rocks, the potential of this mineral for provenance research were first established by Blatt (1967) and Force (1976). Darby (1984) used this method to differentiate the origin of various deposits of coastal Virginia and the variation among the drainage basins with the aid of statistical methods. Similar techniques were used to determine the major fluvial contributor of the US Atlantic shelf (Darby, 1990) and quaternary beach sediments (Darby and Evans, 1992). Morad & Aldahan (1982; 1986) argued that diagenesis could alter the chemical fingerprints in a sedimentary unit. The viability of this method was stressed by Basu and Molinaroli (1989). Anand & Gilkes (1985) investigated the weathering of ilmenite along the weathering profiles of laterites. Morad & Aldahan (1986) studied the alteration of ilmenite under various chemical environments and their trace element variation. Grigsby (1992) established the threshold limits of certain trace elements in ilmenite depending on the petrogenesis of the source.

Gibb et al (1969) carried out the Mössbauer analysis of natural ilmenite samples from throughout the world and suggested this method as a
quick and simple method of determining the weathering undergone by the mineral samples. The efficiency of this relatively new technique is described by Ahmed et al (1992), who determined the exsolution mineral phases of ilmenite of Cox's Bazar beach, Bangladesh.

Sinha (1979) argued that the solubility of ilmenite concentrates varies depending on the degree of alteration undergone by the ilmenite grains. Hoselmann (1987) and Välimaa (1993) pointed out that the fine-grained nature of the alteration products of ilmenite could cause problems during the titania production process. Hayes (1985) and Chernet (1999) used microscopic observations of the textural relationships of the different alteration phases in ilmenite grains, complemented by chemistry to highlight the importance of these analyses on understanding the suitability of the ilmenite ore to different processing techniques.

The microscopic examination and interpretation of the mineral and the delineation of the weathering environments involved were undertaken by several authors (Ramdohr, 1959; Morad & Aldahan, 1986; Frost et al, 1983; Darby, 1984, Darby et al 1985; Hugo & Cornell, 1991; Mucke and Chaudhuri, 1991; Grigsby, 1992).

2.2 ILMENITE RESEARCH IN INDIA

The provenance of the southwest placer deposits has been a matter of dispute since the earliest attempts of investigations in this direction. Gillson (1959), who did a pioneering study of these deposits, suggested basic rocks as the likely source of the deposits. However, subsequent authors (Krishnan, 1968; Subrahmanyam and Rao, 1980), based on the geographical location of the deposits and the lithology of the hinterland pointed to the rocks of the khondalite-charnockite suite as the source. Soman (1985) attributed the khondalite migmatite complex of southern
India as the source rocks of the south west coast placer deposits, and from petrographical observations linked the origin of ilmenite to the action of alumina rich solutions on biotite, which was related to the migmatitisation phase of the region. Bhattacharyya et al, (1997), based on the low Mn/Mg (1.32-2.92) ratios for the ilmenite of these deposits suggested a more basic parentage.

Except for some isolated attempts, a critical and systematic analysis of this important mineral, ilmenite, is yet to be brought out in a comprehensive manner in India. Viswanathan (1957) reported on the black sand deposits of southwest coast and outlined the variation of properties like magnetism of ilmenite. Rao and Rao (1965) and Mallik (1986) carried out a detailed study of ilmenite of Kerala including microscopic evaluation. Mallik (1986) identified the different micromorphological features and explained their formation to solution activity, chemical reaction and mechanical impact during transportation. Ilmenite alteration and the study of its associated intermediate phases were carried out by Subrahmanyan et al (1982) using X ray and Mössbauer analyses. They identified a two-stage model of weathering for ilmenite of Manavalakurichi deposit and observed that magnetism of the mineral increases during alteration and then decreases after reaching the pseudorutile stage. Suresh Babu et al (1992; 1994) undertook the varietal studies of ilmenite, including chemistry, magnetism and specific gravity. They investigated the chemical variation of the different magnetic fractions of ilmenite and concluded that the alteration has succeeded in altering low magnetic fractions of ilmenite to the pseudorutile stage in Manavalakurichi placers.

However, the Manavalakurichi ilmenite, as a whole could be labelled as belonging to the hydrated ilmenite stage (Nair et al, 1995). In Chavara deposit, on the other hand, weathering has reached a more advanced
phase of the pseudorutile stage (Ramakrishnan et al, 1997). The alteration patterns of ilmenite may be along, either 1) continuous, with the formation of intermediate phases before the ultimate formation of rutile; or 2) the discontinuous series, whereby the ilmenite alters directly to rutile, or both simultaneously (Chaudhuri & Newsley, 1990). In the southwest placer ilmenite, intergrowths of mineral phases could not be noted, unlike in the case of Vishakapatnam and Gopalpur ilmenite. This was further confirmed by the application of Mössbauer techniques in the study of the mineral (Suresh Babu et al, 1994). The ilmenite of Ratnagiri deposit was analysed for its chemistry by Sukumaran and Nambiar (1994) in relation to the other ilmenite occurrences of India. They argued that, given its similarities with the ilmenite of the southwest coastal placers, the Ratnagiri ilmenite could be considered a good quality raw mineral for industrial processing.

2.3 ILMENITE BASED INDUSTRY

The economic and industrial significance of ilmenite lies in its role as the most common ore of titanium. The increasing significance of titanium and titanium based products in the industrial spectrum in recent years, from the manufacture of pigments and paints to its use in aerospace/defence industries, underscores the importance of the mineral and the intense research currently on in the industrial world for the characterization of the ore and updating of the processing technology.

2.3.1 Industrial forms of titanium minerals

2.3.1.1 Natural ilmenite: Ilmenite and its product leucoxene are used widely in the welding rod industry as slag formers and modifiers in flux formulations. The low ferric oxide content is the main criterion, which finds use in the industry. Recently a form of reduced ilmenite called
"ferutil" is being used in the welding electrode industry. Ilmenite is also used in sand blasting operation and as a weighing agent in oil industry.

2.3.1.2 Titanium metal: About 4% of the annual production of titanium minerals are used in the production of the metal. In India, this capability is very limited though the Nuclear Fuel Complex is producing sponge titanium in a small scale. There are three stages in the initial production of titanium metal. The initial stage is the production of TiCl₄ by the reduction and chlorination of rutile or synthetic rutile (upgraded ilmenite). The second stage is the reduction of TiCl₄ in the presence of Mg (Kroll process) or Na (Hunter) process. The impure sponge titanium thus formed is treated to acid leaching or vacuum distillation. The extraction of metal titanium involves special techniques such as double ore melting or electrolysis.

The aerospace industry accounts for 45% of the total metal consumption where it is used for the manufacture of air frame structural parts and in jet engine components. The high strength/weight ratio and ability to maintain its mechanical properties at elevated temperatures are the properties, which move it suitable for the above uses.

Because of its high corrosion resistant properties and non toxic nature, titanium finds extensive use in chemical industry and desalination plants, marine machinery and fittings, deep water research, storage tanks, heat exchange units, electricity generating plants, prosthetic devices such as heart pace makers and in oil and gas industry. It is an important alloying element and a effective deoxidizer and cleaning agent in metallurgy. Ferro titanium (15-45% Ti) is a widely used alloy. In ceramic industry Ti is used for producing colored glasses and enamels.
2.3.1.3 Manufactured Titanium dioxide: At the beginning of this century TiO$_2$ was almost exclusively used for the manufacture of pigments and paints. Now the manufacture and production of TiO$_2$ has become very specialised in that different grades of titania are used for specific products. This includes plastics, paper, cosmetics, rubber and pharmaceutical industry, to name a few.

The Titanium dioxide was manufactured commercially only in 1916, but the total consumption now exceeds 2 million tons/year. The properties which make this product so important in industry are its high refractive index, which imparts high opacity, high reflectivity, which gives a high degree of brightness and brilliance, chemical inertness, which gives rise to high colour retention capability, thermal stability over a wide range of temperature, non toxicity, non fibrogenic nature etc.

Two types of manufactured TiO$_2$ are available in the market -‘anatase’ and ‘rutile’ grade. The applications in the industry are different, depending on the end products required. The ‘rutile’ grade is suited to products like paints, printing inks, plastics, cosmetics etc. Anatase grade finds application in paper industry, latex, rubber, pharmaceutical products and soap industry. About 62% of the total TiO$_2$ produced go into the paint industry. Plastic and paper manufacture consumes almost the rest of the pigment produced. TiO$_2$ are used to produce gemstones synthetically.

2.3.2 Upgradation of raw ilmenite

Three processes are generally used for synthetic rutile manufacture from raw ilmenite.
2.3.2.1 Thermal reduction (Smelting): This essentially involves the high temperature oxidation of ilmenite to form pseudorutile structure. The pseudobrookite is treated to solid-state reduction using carbon. Finally, the aqueous oxidation of metallic iron forms hydrated oxide and the upgraded ilmenite is separated out. This process is used by a number of companies like Richards Bay Minerals of Australia and Nissho Inai Corporation of New Zealand.

2.3.2.2 Reduction/oxidation/leaching/Rusting (Becher process): These processes involve a series of oxidation and reduction reactions, which break down ilmenite to TiO$_2$ and iron fractions. The titanium oxide is separated out by the leaching away of iron. This process yields almost pure TiO$_2$. Various variants of this process were developed by different agencies like CSIRO, Australia, Benilite Corp, Ishihara Sangayo, Japan.

2.3.2.3 Reduction/Chlorination: The ilmenite is reduced and subsequently chlorinated to produce a very high grade synthetic rutile (95-98% TiO$_2$). The iron chlorides are removed and oxidised to produce chlorine. Various agencies like Mistubishi Minerals, Japan and Iron Chemicals, Canada use this process for ilmenite upgradation.

Though endowed with some of the largest and high quality deposits in the world, India still imports part of the titanium pigment for domestic consumption. Moreover, India still has a long way to go before it can join the select group of countries with the capability to produce sponge titanium. A limited sponge production is being carried out in Nuclear Fuel complex, but till now it is not viable in the commercial scenario. Although the commercial production of Ti is only a few decades old, the application of the metal range from the manufacture of chemical to the aerospace/defence sector. In the developed world, the manufacture of pigment has become very product specific, i.e., different grades of the TiQ
is manufactured suited to various end products. The production of value added products of ilmenite could yield valuable foreign exchange for the country. At present the bulk of the ilmenite that is produced is being exported at a rate of Rs.2700 per tonne, while we import the finished products, straining the economy.

This calls for the characterisation and grading of the ilmenite ore, which could be used to produce different grades of pigment, based on the impurities present and the iron content. The extractive techniques in the country need to be updated depending on the physical and chemical characteristics of each deposit.

2.3.3 Manufacture of titania pigment

The TiO₂ pigment is manufactured by the following processes.

2.3.3.1. Sulphate process was developed at the beginning of this century. This involves the leaching of ilmenite or titanic slag with con H₂SO₄ and heating by steam. The resultant soluble sulphates of Ti and Fe are dissolved and passed over scarp Fe to convert ferric sulphate to the ferrous form. The resultant solution is clarified and precipitated out as 'Copperas'. The titanyl sulphate containing liquid is hydrolised by injection of steam and an anatase grade or rutile grade Ti pigment is produced. The recovery range is about 85% TiO₂ depending on the titanium content of the feed material. This process has the disadvantage of the high consumption of H₂SO₄ and the problems of disposal of the large amounts of the work products formed like sulphuric acid and iron sulphates. This process is being phased out in developed nations. The Travancore Titanium Products uses this technology for the pigment manufacture.
2.3.3.2. The chloride process: was developed in 1956 by Dupont. The
feedstock consists of rutile or synthetic rutile since using ilmenite cause
problems in the disposal of the large amounts of iron chloride formed.
The feedstock is chlorinated at 950°C in the presence of oxygen and a
carbon source forming Ti and iron chlorides. The TiCl₄ formed is
separated, purified and then oxidised. The recovery is about 90% TiO₂.

The production of a large amount of waste product during the processing
of ilmenite to TiO₂ pigment posed problems in waste disposal and
pollution hazards. So high TiO₂ containing substances like rutile or
upgraded ilmenite is generally preferred as raw material for the pigment
manufacture. The scarcity of rutile, has led to the usage of synthetic
rutile and titanic slag as the feedstock in pigment production.

2.3.4 Titanium based industrial concerns in India

Indian Rare Earths: The Indian Rare Earths Ltd. has plants in Quilon
(Kerala), Manavalakurichi (Tamil Nadu) and Chatrapur (Orissa), in
addition to a Rare Earth plant at Alwaye. The current capacity of the
Quilon plant is 13,00,00 tons of ilmenite/year. Though the Chatrapur
plant was commissioned with a planned capacity of 220,000 tons/year,
due to certain technical problems involved in the processing of the Orissa
ilmenite, the production at present is not up to the expected levels,
though synthetic rutile is produced at a rate of 25,000 m. tons/year
(AMD, 2000).

Kerala Minerals & Metals Ltd. (KMML): In the 1980’s the KMML was
established with a Benilite type plant for the manufacture of synthetic
rutile. The expected capacity was 30,000 tons/year. The company is also
producing TiO₂ pigment using the chloride process at a rate of about
22,000 tons/year. This plant owned by Kerala government is now
preparing schemes for expanding its activities both for ilmenite mining and beneficiation.

Travancore Titanium products (TTP): This is a concern of Govt. of Kerala, which started functioning in 1950. The initial capacity was 1800 tons/year, which have been expanded to the present capacity of 30,000 tons/year subsequently. The company uses the sulphate process for the production of pigment and the wastes are discharged to the Arabian Sea.

Dharangadhara Chemical Works Ltd: This company is situated at Sahupuram near Tirunelveli. It was commissioned in 1970 and is the first one in the world to produce synthetic rutile. The plant uses the Benilite process. The present capacity is about 12,000 MT/year. The synthetic rutile produced contains about 90% TiO₂.

Cochin Minerals & Rutile Ltd.: This concern has started producing synthetic rutile with a moderate capacity, from 1990. The company makes use of Benilite technology for the upgradation of Chavara ilmenite to synthetic rutile. The products in this plant are earmarked exclusively for export.