

Titanium Geology and Metallurgical Processes from Applied Petrologic Viewpoints

Won Choon Park

Abstract: Mineralogy, beneficiation, and processes of titanium ores are reviewed from petrographic viewpoints.

The most important titanium minerals are ilmenite (FeTiO_3) and rutile (TiO_2). Ilmenite will play major role for raw material, because rutile are rapidly diminishing. Thus, there is a need to develop a successful process for producing high grade TiO_2 from ilmenite. Commercial, as well as R and D processes to treat more abundant ilmenite ores fall in three general classes:

1. Iron in ilmenite is partially or completely reduced and separated either physically or chemically.
2. Iron is reduced to ferrous state and chemically leached away from the titanium.
3. Ore is treated to make chlorides either selectively or with subsequent separation and purification of TiCl_4 .

Routes and efficiencies of these process technologies are primarily influenced by the particular ore deposit to be mined and secondly by environmental considerations. One deposit parameters which influence ilmenite process technologies are:

1. Complexity of microtextures of ilmenite intergrown with Fe-oxide minerals.
2. Composition of concentrates; ilmenites contain minor amounts of substituted Mg, Mn, and V. These elements plus iron and gangue minerals can cause difficulties to complete reactions, substantial acid consumption, difficulties of removing waste solids, and waste disposal problems.

Major contributions to be made by petrologists for process optimization are: characterization and interpretation of compositional and physical changes of raw materials and solids derived from process streams. These informations can play significant role in selecting and improving process steps for titania production.

1. Brief review on titanium deposits

1.1. Constitution

Primary titanium deposits occur in monomineralic anorthosite*, gabbro and norite. The ores show substantial mineralogical and chemical variation both within and between individual ore bodies. The "ore" assemblage found in igneous association includes magnetite (Fe_3O_4), hematite (Fe_2O_3), maghemite (Fe_2O_3 with spinel structure), ilmenite (FeTiO_3), ulvite (Fe_2TiO_4), rutile (TiO_2), a variety of spinels poor in Fe and Ti, minor sulfides, and apatite [$\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$]. Microstructures of ore minerals are governed largely by solid-solutions in Fe-Ti-O system, as discussed in the mineralogy section. Because of the large mechanical and chemical stability under the surface con-

ditions of the earth and the high density, ilmenite, Ti-magnetite and rutile sands concentrate as placers on the beach and the alluvial deposits. Figure 1 depicts geological environments where titanium is concentrated, so that mining is economical.

Of the two economically important titanium minerals, ilmenite (FeTiO_3) and rutile (TiO_2), the former accounts for about 85% of the world's raw materials requirements for TiO_2 pigment. Role of ilmenite will grow, because by 1980's reserves of high grade rutile sands can be exhausted.

1.2. Geochemistry and mineralogy

1.2.1 Introduction

Tetravalent titanium is the most common and stable state of titanium in natural minerals. The ionic radius of Ti^{4+} is 0.68 Å. With the radius ratio of 0.52 for Ti^{4+} and O^{2-} , titanium is expected to be octahedrally coordinated by

* Igneous rocks, almost entirely composed of plagioclase feldspar.

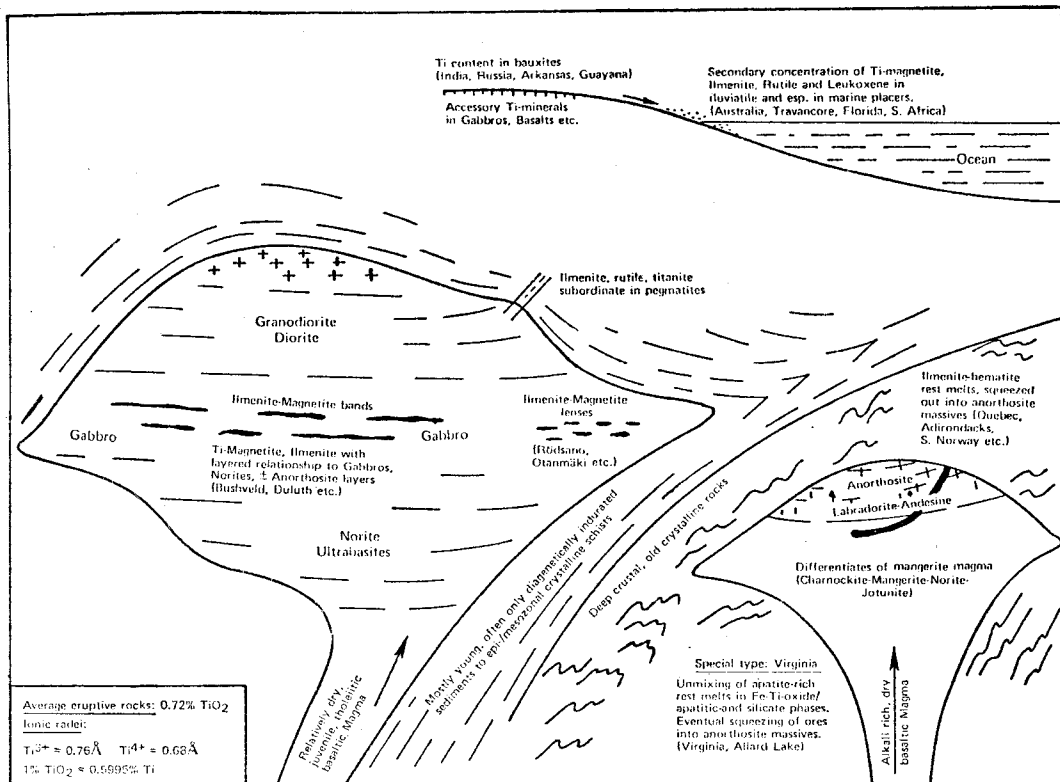


Fig. 1 Genetic survey of titanium deposits

oxygen. Divalent titanium does not occur in natural minerals. Existence of trivalent titanium in natural minerals is questionable.

Titanium plays an important role in many oxides and silicates. Among the known, over 140 titaniferous minerals containing $>1.0\%$ Ti, only ilmenite (FeTiO_3), Ti-magnetite (Fe_3O_4 with varying Ti content), and rutile (TiO_2) are economically important. Other titaniferous minerals are only of mineralogical and geochemical interests. Ti^{4+} can substitute for Mg^{2+} , Al^{3+} , Cr^{3+} , Sn^{4+} , Zr^{4+} , Nb^{5+} and Ta^{5+} in minerals.

The most wide-spread and important substitutional relationships of titanium are found in the system Fe-Ti-O (Fig. 2). Complete solubility between magnetite-ulvite, as well as, ilmenite-hematite occurs because of the analogous

crystal structures at plutonic temperature ranges ($>7-800^\circ\text{C}$). For the ilmenite-magnetite pseudobinary system, only limited solubility occurs. Ore microscopic observations of thin ilmenites in magnetites along (100) and (111) indicate subsolidus oxidation of homogeneous magnetite-ulvite solid solutions (Buddington and Lindsley, 1964).

Primary deposits of titaniferous iron are known such as at Allard Lake (Quebec), Tahawus (New York), Tellnes (Norway) and Otanmaki (Finland). Their relative commercial value depends not only on the TiO_2 content, but also on the liberation size of the titanium minerals. This factor is a function of the relative quantities of Fe_2O_3 , Fe_3O_4 , and TiO_2 present; ilmenite is present as a discrete phase only if its quantity exceeds the solubility of FeTiO_3 in

magnetite.

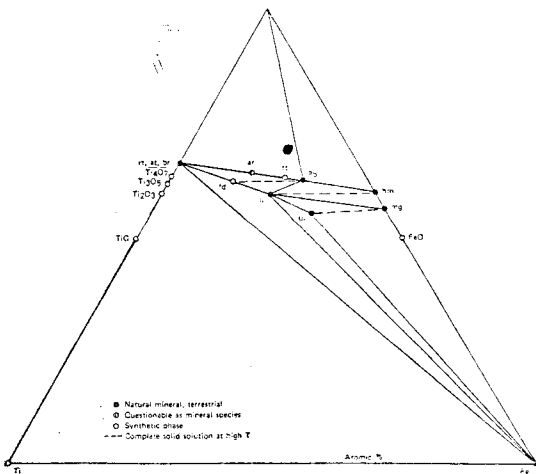


Fig 2. Compatibilites in the system FeTiO
 ar: arizonait-eF₂Ti₃O₉ (?)
 at: anatase-TiO₂
 br: brookite-TiO₂
 fd: ferrous distanate-FeTiO₂ [armalcolite. (Fe_{0.5} Mg_{0.5}) Ti₂O₅, a new mineral from the Apollo 11 samples, occurs together in contact with il.]
 hm: hematite-Fe₂O₃
 il : ilmenite-FeTiO₃
 mg: magnetite-Fe₃O₄
 Pb: pseudobrookite-Fe₂TiO₅
 rt : rutile-TiO₂
 tt : tetragonal titanate-Fe₄Ti₃O₁₂
 ul : ulvöspinel-Fe₂TiO₄

1.2.2 Mineralogy Ilmenite

Chemical composition: Ilmenite's theoretical TiO₂ content is 52.8%, but many ilmenites

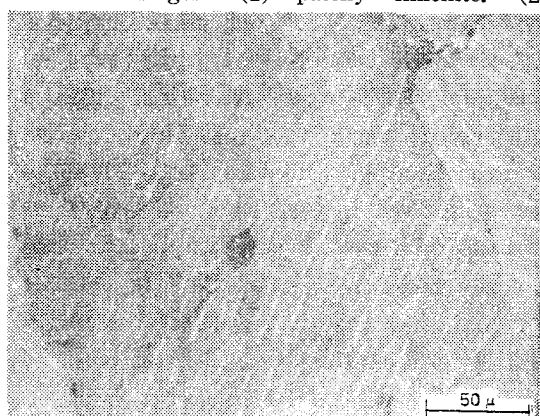
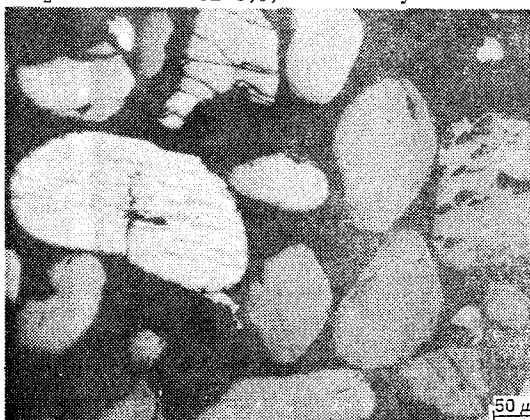


Fig 3. Exsolutions of hematite (light grey to white) and ilmenite (grey to dark grey).
 Right: Hematite is exsolved out along basal planes of ilmenite. Abu Galgua, Egypt.
 Left: Ilmenite sands. All grey grains are ilmenite. Grain on the center right has hematite lamellae and the one on the center left, ilmenite is exsolved out of hematite. Richard Bay, S. Africa.

contain various TiO₂ values ranging from 47 to 70% due to substitutions by other elements and to alteration.

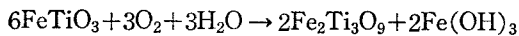
The formula of ilmenite is more fully expressed as (Fe, Mg, Mn) TiO₃ with only limited amounts of MgO (up to 3.4%), MnO (up to 1.5%). FeTiO₃ usually contains considerable amounts of Fe₂O₃, which at high temperatures is completely miscible (Gray et al., 1974); at low temperature has only limited solubility in ilmenite. In many ilmenities, excess Fe₂O₃ occurs as minute exsolution lamellae of hematite as temperature of the rock is lowered after crystallization (see Fig. 3). Amount of Fe³⁺, Mn and Mg in ilmenite greatly influences the phases to be formed during process streams and the selective removal of iron from ilmenite in titania processes.

Ilmenite often occurs in association with magnetite and in such rocks the ilmenite is preferentially enriched in Mn and Mg. Geikielite, MgTiO₃ and pyrophanite, MnTiO₃ are isostructural with ilmenite. Cr, Ni and V all tend to be concentrated in the magnetite in such coexisting pairs of ore minerals.

Alteration: Ilmenities are often altered and, as their iron content decreases, go through three alteration stages: (1) "patchy" ilmenite. (2)

amorphous iron-titanium oxide, and (3) leucoxene. Leucoxene is normally fine crystalline rutile. Degree of alteration should play an important role in process options and streams, because of their differences in composition, structures and textures.

Many altered ilmenites from beach sand deposits are comprised of the mineral pseudorutile, a highly disordered oxidation product of ilmenite that represents the composition at which all ferrous iron is oxidized to ferric, with concomitant leaching of one-third of the iron in the ferric state, e. g. :



Further removal of iron results in the destruction of the structure and the formation of rutile.

Crystal structure: On the basis of the close similarity of its x-ray power pattern with that of hematite, Ewald and Herman (1931) predicted that ilmenite would have essentially the same structure as hematite. Compared to the hematite structure (Fig. 4), one-half of the Fe ions are replaced by Ti in such a way that every Fe-O₃-Fe unit becomes a Fe-O₃-Ti unit, and the sequence of cations along any [0001] axis is ... Fe-Ti-□-Ti-Fe-□-Fe... where the hyphens represent intervening planes of oxygen layers. As in hematite, every third potential octahedral site is empty; the nearest cation to an empty site along [0001] are always two Fe or two Ti (Fig. 4). The Fe-O₃-Ti unites are so arranged in (0001) that oxygen layers alternate with metal layers, which themselves alternate between layers of Fe and layers of Ti. As in hematite, the metal layers are separated by planes of oxygens. The sequence of metal layers in ilmenite is somewhat similar to the magnetic structure of hematite: the Fe planes correspond to the A substructure and the Ti planes to the B substructure.

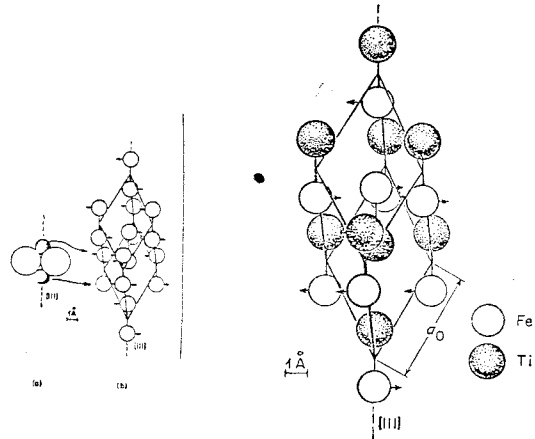


Fig 4. Crystal structures of hematite (left) and ilmenite (right).

Hematite: (a) Fe-O₃-Fe "pseudo-molecule". The "triplets" of three oxygens (large spheres) are essentially closed-packed and lie in the (001) plane (= (0001) plane, hexagonal axes). (b) Rhombohedral cell of hematite. Each corner and the center of the unit rhombohedron is occupied by the center of a Fe-O₃-Fe unit; the oxygen "triplets" are omitted for clarity. The magnetic structure is indicated schematically by the arrows: all Fe³⁺ ions in a given (111) layer have parallel spins but are antiparallel to those of the adjacent layers.

Ilmenite: Rhombohedral cell of ilmenite. The oxygen triplets are omitted for clarity. Along [111], layers of cations alternate with layers of oxygens; of the cation layers, layers of Fe²⁺ alternate with layers of Ti⁴⁺. Below the Neel temperature (55°K) all Fe²⁺ spins lie in (111) and are antiparallel in adjacent Fe layers, as indicated schematically by the arrows.

Magnetic structure: At room temperature pure ilmenite is essentially paramagnetic, but at sufficiently low temperature it becomes anti-ferromagnetic.

Rutile

Chemical Composition: Although rutile is essentially TiO₂, some reported analysis show considerable amounts of both ferrous and ferric iron and rarely major of niobium. In a few cases, the iron could be due to intergrowth of ilmenite but the close similarity in ionic radius between Ti⁴⁺ and both Nb⁵⁺ and Ta⁵⁺ enables the latter to enter TiO₂, the structure being electrostatically balanced either by vacancies ir

some lattice positions, or by the complementary substitution of divalent ions such as Fe^{2+} .

Crystal structure of rutile, anatase and brookite: Structures of the three TiO_2 polymorphs—rutile, anatase and brookite—are discussed together to emphasize the similarities and differences between them. Brookite is orthorhombic, whereas the others are both tetragonal with $c/a < 1$ for rutile and > 1 for anatase.

In both structures of rutile and anatase, Ti is coordinated by six oxygens, and each oxygen by three titaniums; the difference is the sequence of the coordination octahedra. In rutile, only two edges of the octahedra—those lying in (001)

are shared (Fig. 5a), whereas in anatase four edges are shared. In rutile the octahedra form chains parallel to [001]; the chains are linked by the sharing of corners. In anatase, on the other hand, there are no distinct chains (Fig. 5b).

Values of the unit cell dimensions for rutile are $a=4.59373 \pm 0.00005 \text{ \AA}$, $c=2.95812 \pm 0.00005 \text{ \AA}$. For anatase, $a=3.785 \pm 0.0001 \text{ \AA}$, $c=5.14 \pm 0.0006 \text{ \AA}$.

The structure of brookite is considerably more complex than those of rutile and anatase (Fig. 5c). The deformed coordination octahedra form staggered chains that are cross-linked by shared-edges. The Ti ions are slightly displaced from the centers of the octahedra. Unit cell dimensions are $a=9.174 \pm 0.001 \text{ \AA}$, $b=5.456 \pm 0.002$, $c=5.138 \pm 0.002$.

Upon heating under reducing conditions, rutile first loses oxygen (TiO_{2-x}) and then converts to a host of other phases that are termed Magneli phases.

2. Beneficiation

Placer deposits: Dredge or draglines are used for mining. Heavy mineral fractions are first separated by wet gravity methods with Humphrey spiral. Final concentrate is separated by electrostatic and magnetic methods. Recovery is normally 80–90%.

Igneous rock deposits: (1) Ore is crushed and ground to 28 mesh. Magnetic fraction is removed by low intensity wet magnetic separator. An ilmenite concentrate is made by flotation, containing about 45% TiO_2 . The concentrate is sintered to yield a blast furnace feed.

(2) Some ores cannot be separated by mechanical means, such as at Allard Lake. Ore, containing 35% TiO_2 , is crushed, mixed with coke, and is fed to electric arc furnace to yield pig iron and Ti-slag containing 70–83% TiO_2 .

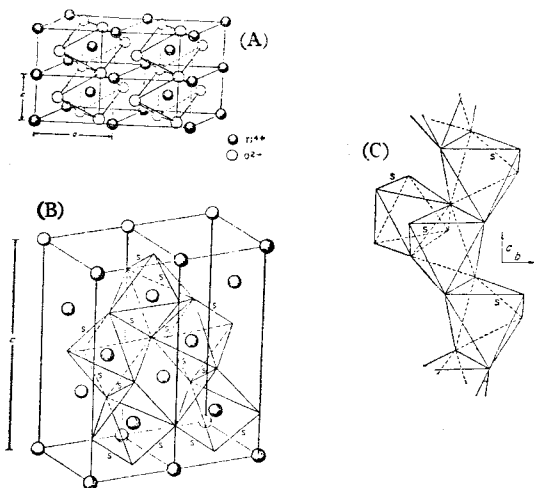


Fig 5. Crystal structures of rutile (A), anatase (B), and brookite (C).

Rutile (A): Four unit cells showing the coordination octahedra of oxygens about the Ti at center of each cell. Only those two edges of the octahedra that lie in (001) are shared with adjacent octahedra. The shared edges are shorter than the unshared edges.

Anatase (B): Two unit cells of anatase showing distorted octahedra of oxygens about Ti. The oxygens are omitted for clarity; their centers lie at the apices of the octahedra. The front halves of two lower octahedra are omitted; they lie in front of the two cells illustrated. The shared edges (S) are shorter than the unshared edges.

Brookite (C): Part of the brookite structure, showing a chain of distorted coordination octahedra of oxygens about Ti's. Each octahedron shares two edges with two octahedra in the chain and a third edge with an octahedron—one of which is shown—of an adjacent chain. Other shared edges are shown by S.

3. Current commercial processes

3.1 Processes of Rutile substitutes

Rutile substitutes are materials having a TiO_2 content approaching that of natural rutile, but made from ilmenite.

Most processes involve the removal of iron oxide ilmenite to leave a titania-rich residue.

The processes fall into three general classes:

1. Iron in ilmenite is completely reduced by use of carbon or hydrogen and separated from the reaction mass either physically or chemically (such as QIT process and Western Titanium process).
2. Iron is oxidized to ferrous state at 950° and 800°C respectively and chemically leached away from the titanium at 105°C (such as Murso process).
3. Ore is treated to make chlorided either selectively or with subsequent separation and purification of TiCl_4 .

The reason for oxidizing ilmenite first in process 2 above is to eliminate sintering of

grains, i. e., to get away with forming wustite. (FeO) or iron on the grain surface, if reduced directly. Also oxidation and reduction enhance leaching of iron from the reduced ore.

3.2 Process of pigment production

Pigment is produced commercially by two methods which require different raw materials. Seventy to eighty percent of the Free World pigment production capacity uses "sulfate process" and the rest "chloride process". Most new pigment in the United States use the latter process because of the environmental considerations.

1. In the "sulfate process", finely ground ilmenite is reacted with hot sulfuric acid, a portion of the contained hydrated ferrous sulfate is crystallized and removed, and titanyl sulfate is hydrolyzed, precipitated, filtered, and calcined to produce the desired crystal form and particle size. Recovery of titanium dioxide is about 77%. Large quantities of waste in the form of sulfate and H_2SO_4 make this process environment-

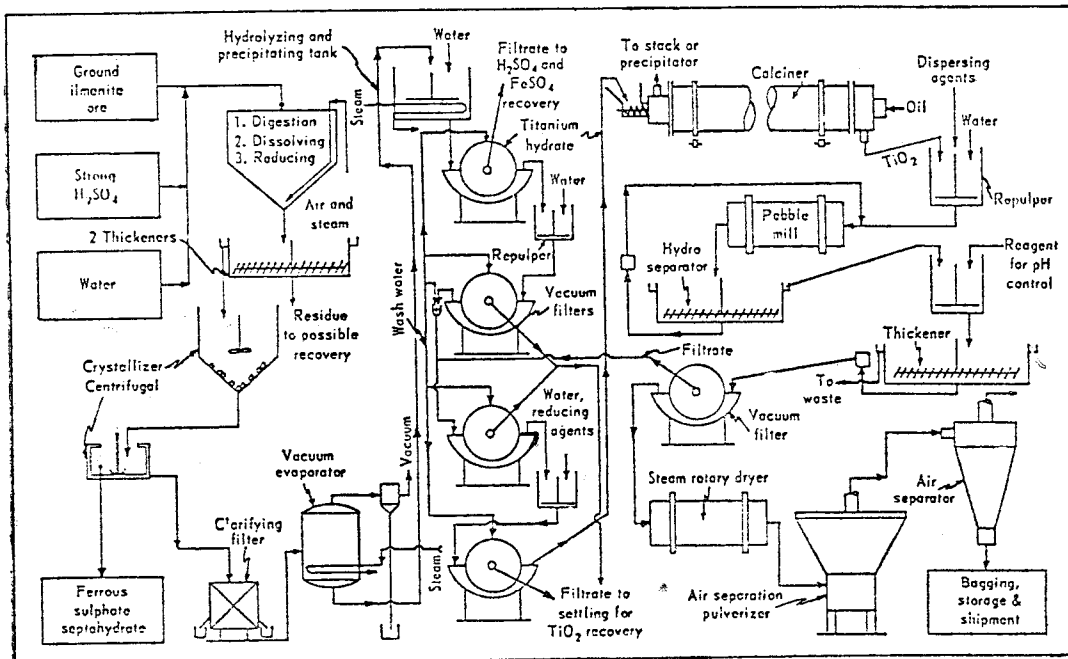


Fig 6. Flow sheet of the manufacture of titanium dioxide pigments. (After Barksdale, 1966, p. 214.)

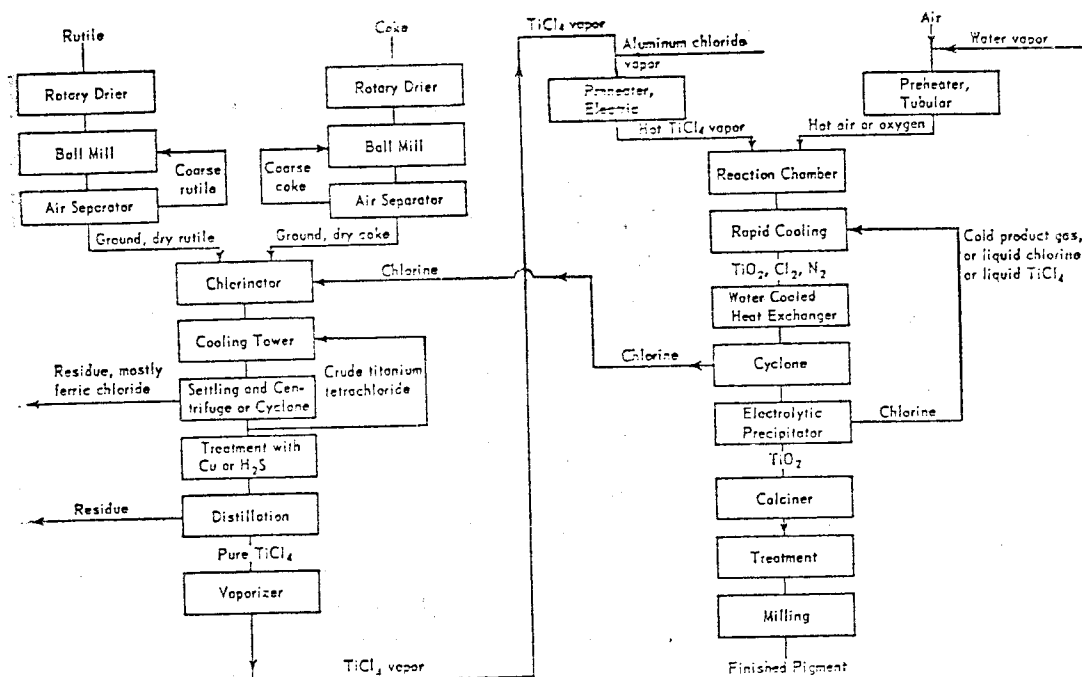


Fig 7. Flow sheet of the chloride process for the manufacture of titanium dioxide pigment. (After Barksdale, 1966, p. 482)

ally undesirable. Figure 6 shows typical flow sheet of most plants of this process for the manufacture of TiO_2 pigment.

- In the "chloride process", rutilite is converted to titanium tetrachloride in fluid-bed chlorinator at $850^\circ\text{--}950^\circ\text{C}$ in the presence of petroleum coke. Rutilite is the preferred raw ore, although ilmenite can be used; ilmenite causes excessive chlorine consumption and leads to ferric chloride waste disposal. TiCl_4 is oxidized with air or oxygen and calcined at $500^\circ\text{--}600^\circ\text{C}$ to crystallize TiO_2 and to remove residual chlorine. Recovery is about 89%. This process is favored because it produced less effluent and is cheaper to operate. Figure 7 shows flow sheet of this process.

3.3 Process of metal production

Titanium sponge metal is produced commercially by the Kroll process, in which purified TiCl_4 is reduced with magnesium or sodium under an inert atmosphere. MgCl_2 or NaCl contaminants is leached. The sponge is com-

pressed and made into ingot by two or more successive vacuum arc-melting operations.

3.4 "Capel Process" of western titanium, Australia

The ilmenite feed is first pre-oxidized in a rotary kiln, where it is converted to a mixture of ferric pseudobrookite (Fe_2TiO_5) and rutilite. This material is fed hot to a large rotary kiln, where it is mixed with coal char or coal and reduced at a final temperature of 1200°C . In the reduced product the grain structure persists, but each grain is converted to an interlocking mixture of iron crystallites and titanium-rich oxides.

In 1970, CSIRO of Australia began systematic investigations of reduction stages to better understand and to improve process steps; these investigations included: chemical, structural and phase equilibria studies, kinetics and mechanisms of reduction of pre-oxidized ilmenites (series of papers of this effort are published). CSIRO phase equilibria study showed that once most of the iron in the natural ilmenites is

reduced to metal, the phase equilibria are governed by the system $\text{MnO-FeO-TiO}_2\text{-Ti}_2\text{O}_3$. About 92% of the total titanium was tied with MnO and FeO as M_3O_5 solid solution (where $\text{M}=\text{Ti, Mn, Fe}$). Lowering of oxygen fugacity of the kiln by the use of pre-dried feed from 10^{-14} atm to 10^{-15} atm resulted in high grade reduced titania (Magneli phase) and iron. However, Mn and Mg originally tied in ilmenite structures promote the stabilization of the M_3O_5 phase. This phase contains considerable amount of iron, is not attacked in the subsequent correction process, and thus lowers the purity of the upgraded material.

A considerable gain in purity of upgrade may be achieved in ilmenite beneficiation processes that utilizes reduction to metallic iron, if Mn and Mg can be segregated from the feed either before or during the reduction steps possibly in the form of sulfides.

4. Current research and applications

Several hundred papers and patents are known. However, advances in titanium metallurgy is likely to come mainly from improvement in present processes. The major objective is to develop a successful process for the production of high grade synthetic rutile from ilmenite and expand its use.

Current R&D efforts for upgrading ilmenite to materials suitable for chlorination may be classified into three general categories:

1. The iron oxide content of ilmenite is reduced essentially to the metallic state and is removed subsequently by chemical or physical methods.
2. Most of the undesirable iron and other metal oxides are removed by leaching with acid. Depending on ilmenite composition, a pretreatment such as partial oxidation and or partial reduction of the iron may be required to attain Fe^{2+} prior to leaching.

3. Some or all of the metal contents in the ilmenite are converted by chlorination to their prospective volatile chlorides. Then these are separated into individual compounds or groups of compounds for subsequent processing.

Possibly production of titanium metal may be realized by fused-salt electro-winning and electrorefining.

A few important research projects being conducted to beneficiate abundant ilmenite ores at present are:

1. Kinetics of reduction of ilmenites at elevated temperatures.
2. Aqueous oxidation of reduced ilmenite.
3. Effect of sulfur in a segregation of manganese impurities involving five-component system, Fe-Mn-Ti-O-S . This is aimed to form $(\text{Mg, Fe, Mn})\text{S}$ phase which would upgrade the final titanium oxide purity.
4. In the field of ilmenite flotation, Gutierrez (1976) found that aeration in water or heating in air of ilmenite greatly improve the recovery by flotation with oleic acid, apparently due to oxidation of iron to ferric state on the surface of ilmenite grains.

5. Applied petrology in process improvement

5.1 Introduction

In the mineral industry, most processes occur between solids, or by solids interacting with liquids and gases. Therefore, with the exception of reactions in the molten or gaseous states, the results of mineral processes can only be predicted from empirical data. Lacking an insight into what occurs at the surface and in the interior of particles, empirical data collection has had to follow a "black box" approach, involving costly experimentation on a large scale at several levels of the significant variables and sometimes costly failures.

Modern process petrology supplies such an insight. It permits us to observe specific changes in texture, microstructure, placement and association of substances within aggregates, and physical properties; to relate them to changes in process conditions; and thus, even after only small-scale experiments, to predict process performance and identify optimal conditions.

This type of study has been of great value in the pre-pilot plant and pilot plant development work where the identification of unusual behavior of a particular material means substantial savings in money and time in future processing steps.

Of particular interest is the application of process petrography to the increasingly important field of hydrometallurgical processing. Regardless of how performed—leaching ore in a reactor or in-situ or leaching a concentrate—it involves contacting a heterogeneous mixture of minerals of irregular geometry with a leach solution. Without process petrography it is difficult to gain an understanding of the impact of process changes on the numerous physical phenomena and chemical reactions that occur simultaneously.

5.2 Contribution to Ti process

Petrographic and mineralogical information of a Ti deposit should be used at an early stage of process development, because process options available and their efficiencies are primarily dependent on the raw ore.

Use of petrography can be classified into two categories: (1) characterization of the raw ore to predict process performance; and (2) analysis and interpretation of solids derived from the process streams in order to understand and improve that process.

For each of these categories, the following information should be collected:

(1) Raw ore characterization

- How is Ti content in the ore distributed among minerals in the rock (or sands)? What are the variations in compositions, structures and physical properties of titaniferous minerals? (From this information, optimum process options chosen.)
 - What are the grain sizes, shapes and textures of titaniferous as well as other gangue minerals? (These will determine behavior of ore in various process steps.)
 - Are there any elements (such as Mg, Mn, V, Cr, for example) or minerals which can cause problems in economics and in the process streams? Are these economically separable before feed is processed?
- (2) Solids derived from process streams
- Size, texture, hardness, and intergrowths of phases formed. These properties can influence efficiencies of the subsequent process steps.
 - Compositions of solids. For example, manganese and magnesium ions diffused towards grain boundaries can prevent reaction to complete, as often observed in ilmenite reduction steps. This may be prevented by changing temperatures or eliminating them beforehand.
 - Physical changes such as pores and shape that take place within the solid grains during the reactions. How are these changes effected by reaction parameters in contact with gas or liquid, and will they result in the physical characteristics of the synthetic rutile produced?
 - For high temperature oxidation and reduction of ilmenite ores, information on phase equilibria relations and reaction kinetics are important for process control such as adjusting oxygen fugacity.

요 약

티탄광의 광물학적 성질, 채광상의 유효성 및 처리과정에 의해서 암석학적 관점에서 고찰하였다. 티탄광물로서 가장 중요한 것은 티탄철석(Fe TiO_3)과 루틸(TiO_2)이다. 루틸의 매장량은 급격하게 감소되고 있으므로 티탄철석이 차원으로서 중요한 역할을 하게 되었다. 따라서 티탄철석으로부터 고품위의 TiO_2 를 만드는 데 성공적인 방법을 개발할 필요가 있다. R과 D처리에서와 마찬가지로 상업적으로도 다량의 티탄철석광석 처리하는 방법으로 다음의 세가지가 있다.

1. 티탄철석내의 철을 물리적이거나 화학적으로 부분적으로 혹은 완전히 환원시킨 후 분리하는 법.
2. 철을 제 1 산화철 상태로 환원한 후 화학적으로 티탄늄으로부터 용출시키는 법.
3. 광석을 선택적 혹은 연속적 분리방법으로 염화물을 만든 후 TiCl_4 의 순도를 높이는 법.

이러한 처리기술의 과정과 효율은 채굴하는 광상의 특성에 따라 일차적으로 영향받으며, 이차적으로는 환경의 상황에 의해서 좌우된다.

티탄철석 처리기술에 영향을 주는 광상의 요소는

1. Fe-산화광물과 공생하는 티탄철석의 현미경조직의 복잡성
2. 농축물(정광)의 조성, 즉 티탄철석은 치환성원소인 Mg, Mn, V를 소량씩 함유한다. 이 원소들에 철과 백석광물들을 합하면 여러가지 반응의 완성, 산의 실소모량, 폐기물체물의 제거난점 및 폐기물 처리문제등의 곤란이 야기된다. 암석학자에 의해 공헌될수 있는 최적의 주요과제는 처리과정에서 유도되는 천연물질과 고체물에 대한 성분상의 변화와 물리적 변화의 감정 및 적절한 해석이다. 이러한 지식은 산화티탄생산을 위하여 처리되는 여러 단계에 있어서 그 방법을 선별하고 발전시키는데 중요한 역할을 할수있다.

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