CHAPTER 12.38

Titanium Ores

Thomas P. Battle

The only chemical elements formed in the early years of the universe were hydrogen and helium, with a trace of lithium. All the other elements were created much later, in the cores of massive stars toward the end of their lifetimes.

Stars, such as the Sun, are powered by the conversion of mass into energy as four hydrogen atoms react to form one helium atom. This requires such high temperatures and pressures that these reactions only occur in the centers of stars and provide enough power to light the star for millions, often billions, of years. For small stars, nucleosynthesis ends here—the core of the star never grows hot enough to fuse helium into larger nuclei. The larger the star, the higher the temperature and pressure of its core; stars with an initial mass around that of the Sun will ultimately reach the conditions required for the next stage of elemental development, the triple alpha process, where three ionized helium atoms (alpha particles) fuse to form carbon 12 (Gribbin 2000). At yet higher temperatures and pressures, alpha particles will react with carbon to form oxygen; for stars with masses similar to the Sun, that is as far as it goes. For stars with initial masses larger than approximately eight times that of our Sun, however, even higher temperatures and pressures permit fusion to higher mass nuclei. The most common sequence of events leads to nuclei formed by the addition of alpha particles to carbon or oxygen atoms. These form, in turn, neon, magnesium, silicon, sulfur, argon, calcium, titanium, chromium, and iron (heavier elements are formed only during the last brief moments of a massive star's life, before it becomes a supernova). These elements are dispersed to the interstellar medium at the end of the star's lifetime and become available for the next generation of stars (Gribbin 2000).

It was in the cold of space that the various elements formed solids, and the first minerals were created. It is believed that the earliest mineral formed was diamond (Hazen et al. 2008), followed by oxides (first aluminum oxides, then by Ca, Ti, Ni, Fe, Mg, and Si), and then silicates (Gribbin 2000).

According to Chown (2001):

> Nobody knows for sure how many times this cycle of cosmic death and rebirth was repeated before a cold cloud of gas and dust on the outskirts of the Milky Way began to slowly shrink under its own gravity 5 billion years ago. The cloud had hung in space, inky black against the background stars, for tens of millions, perhaps hundreds of millions, of years. What set it in motion was not certain. Perhaps it was the impact of debris from a nearby supernovae. Once it began shrinking, however, there was no stopping it. In time, the heavy elements in the cloud became incorporated into the newborn sun and its entourage of planets. They became incorporated into the earth and its rocks and ultimately into the first primitive living cells.

Thus, each generation of stars will have slightly higher contents of *metals* (meaning, in astronomical terms, any element beyond helium on the periodic table), depending on the composition of the gas it formed from. The Sun is considered to be at least a third-generation star, since it has a relatively high content of metals, but the Sun is still dominated by hydrogen and helium (Chown 2001). For every 1 million atoms of hydrogen in the Sun, there are 98,000 of helium, 850 of oxygen, 360 of carbon, 120 of neon, 110 of nitrogen, 40 of magnesium, 35 of iron, and 35 of silicon (Choi 2014). On this scale, the number of titanium atoms would only be one or two (Amethyst Galleries 2015). Titanium is relatively more abundant in the earth's crust because of the absence of elements that vaporized away from the forming earth (such as He and Ne), or historically have ended up in the liquid or gaseous state (H, C, N).

MINERALOGY AND MINING OPERATIONS

At approximately 4,400 ppm, titanium is the ninth most common element in the earth's crust (Emsley 2002). Titanium mineralogy is marked by its strong attraction to oxygen, such that titanium is virtually never found in nature in the elemental state. Instead, economic concentrations of titanium are found either in the form of simple oxide ores (based on rutile, nominally titanium dioxide), or combined iron titanium oxides (the basic mineral being ilmenite, $FeO{\cdot}TiO_2$). Both of

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Thomas P. Battle, Extractive Metallurgy Consultant, Self-Employed, Charlotte, North Carolina, USA

these minerals have been identified in meteorites, and thus are among the 60 or so minerals to be present since the formation of the earth (Hazen et al. 2008). The extractive metallurgy of titanium has been defined by the fact that ilmenite ores, of one type or another, are far more common than rutile ores, forcing metallurgists to remove not just oxygen, but a significant amount of iron to make a quality titanium product.

The major minerals of titanium are discussed first, followed by the key structural feature that defines the type of mining operation required, that is, whether the ore deposits in a given situation happen to be in rock or in sand. Finally, typical mining operations are discussed, along with the major producing countries and companies.

Minerals of Titanium

An unusual feature of titanium is that "in many rocks, common silicate minerals rather than oxides contain most of the TiO_2 in the rock. Because only oxide minerals are economically useful at present, the economic geology of titanium is as much a function of mineralogy as it is of chemistry" (Force 1976). Thus, it is not just a matter of looking for regions of overall high titanium content, because that may have nothing to do with economic concentrations of ore.

Rutile

The name *rutile* comes from the Latin *rutilis*, or red (Mindat .org, n.d.). Its nominal composition is titanium dioxide (TiO_2), and it is isomorphous with two other fairly common titanium minerals, brookite and anatase (Pellant 2002). It is formed as an accessory mineral in igneous rocks and either remains in the rocks or is removed from the structure by weathering away of the other components. It is the "most stable of all soil components: They [TiO_2 and titanates] are so resistant to weathering that very little titanium is leached into rivers" (Emsley 2002). Consequently, it often forms a part of a heavy mineral suite in sand deposits. Because of substitutions and intergrowths, the actual composition of rutile is rarely 100% TiO_2; Fe, Ta, Nb, Cr, V, and Sn are common impurities. Typically, there are 3%–5% impurities in natural rutile ores (Iluka 2014; Stanaway 1994; Rozendaal et al. 2010).

Ilmenite

Ilmenite was first identified in rock from the Ilmen Mountains in Russia (Amethyst Galleries 2015). The nominal composition of ilmenite is $FeTiO_3$, but as used in the titanium ore literature, the word *ilmenite* expresses a fairly large range of composition compared to the pure mineral, which is 52.7 wt % TiO_2, 47.3% FeO. In the mining literature, the high TiO_2 composition in ilmenite can reach 67% or even more, because of enrichment during weathering and transport. In fact, at higher TiO_2 contents, "much of this material actually consists of alteration products pseudomorphous after ilmenite" (Force 1976). Examples of minerals commonly defined at higher TiO_2 contents are leucoxene and pseudorutile. Interestingly, although the word *leucoxene* is commonly used in the industry, it is not officially considered to be a mineral; instead it is "a loose term for the end products of this alteration of ilmenite. The titanium is contained in fine-grained aggregates of rutile, brookite, anatase, hematite, and (or) sphene" (Force 1976). Pseudorutile ($Fe_2Ti_3O_9$), however, is an alteration product "in which all the iron has been oxidized to the trivalent state and one-third of it has been leached out" (Grey and Reid 1975). Many of the titanium minerals and pseudo-minerals are listed in Table 1. The following, written more than 40 years ago by Garnar (1972), still seems to apply:

> Because present nomenclature is well established with pigments-oriented geologists, I believe that future workers will continue to call the black, opaque, para-magnetic grains containing less than 65% TiO_2 by the name "ilmenite"; the less magnetic, lighter colored, alteration products containing from 85% TiO_2 to 98% TiO_2 will continue to be called "leucoxene." The primary unaltered rutile grains associated with heavy minerals have always been called rutile—even though some of these grains may be anatase or brookite.

The titanium content of ilmenite ore can also go lower than the pure mineral, because of intergrowths or solid solutions with hematite and magnetite. At the low end of composition, some Fe-Ti compounds grade toward pure magnetite, becoming known as *titaniferous magnetites*. In fact, at the lower end, titanium is a nuisance impurity in ores being mined for their iron, or perhaps vanadium, content (Taylor et al. 2006). More specifically, some sources define a titanomagnetite as a mineral in the solid–solution series between magnetite and ulvöspinel.

Variability in composition of ilmenite is not limited to the wide range in TiO_2 contents; elemental substitutions into the main structure of the ilmenite molecule can occur, either substituting for the iron constituent, or the titanium. Such impurities include manganese, magnesium, and vanadium (Mindat .org, n.d.). Chromium may also be present, sometimes in the form of chrome spinels that are hard to separate from ilmenite using physical beneficiation (Ahmad et al. 2015). In addition, many titanium deposits also contain measurable amounts of

Table 1 Titanium minerals

Mineral	Formula or Range	Comments
Anatase	TiO_2	Isomorphous with rutile
Anosovite	Ti_3O_5	Discredited in 1988 (Mindat.org, n.d.)
Brookite	TiO_2	Isomorphous with rutile
Ilmenite	$FeTiO_3$	Major ore mineral
Leucoxene	$FeTiO_3 \cdot TiO_2$	Not an official mineral, but a composition range*
Perovskite	$CaTiO_3$	—
Pseudobrookite	Fe_2TiO_5	As solid solution in slags, generically given as M_3O_5
Pseudorutile	$Fe_2Ti_3O_9$	Ilmenite weathering product
Rutile	TiO_2	Major ore mineral
Sphene	$CaTiSiO_5$	Also known as titanite
Titanohematite	$Fe_{2-y}Ti_yO_3$	Rhombohedral (Park and Ostrovski 2003)
Titanomagnetite	$Fe_{3-x}Ti_xO_4$	The solid solution mentioned earlier (Hu et al. 2013; Park and Ostrovski 2003); also used as a more general term
Ulvöspinel	Fe_2TiO_4 (or $2FeO \cdot TiO_2$)	Forms solid solution with magnetite

* This definition is from Jones (2009).

Table 2 Analyses of typical titanium ores

	Green Cove Springs Leucoxene	Trail Ridge	Quilon	Capel	Kuranakh	Tellnes	Panzhihua	Allard Lake
Location	United States	United States	India	Australia	Russia	Norway	China	Canada
Type	Sand	Sand	Sand	Sand	Rock	Rock	Rock	Rock
TiO_2, %	76	66	60	54	50	45	38	36
Fe_2O_3, %	21	27	26	18	—*	11	6	28
FeO, %	—	2	10	24	38	35	30	28
CaO, %	—	0.00	—	0.00	—	0.00	0.04	0.00
MgO, %	—	0.003	0.005	0.002	—	0.05	0.06	0.04
SiO_2, %	1.2	0.005	0.008	0.005	0.02	0.02	0.10	0.02
Al_2O_3, %	—	0.014	0.016	0.009	0.03	—	0.02	0.02

Source: Battle et al. 1993

* Dash indicates analyses not supplied, not measured, or below detection.

thorium and radium. Miners and consumers of these ilmenites must watch for concentration of the radioactive species in waste product streams or pipe deposits (McNulty 2007), even if the starting mineral suite is fairly low in thorium and uranium (a common source of radioactivity in mineral sands is the mineral monazite).

A primary formation mechanism for ilmenite is magmatic segregation. Because of the comparatively high levels of titanium, iron, and oxygen in some magmas, ilmenite precipitates early in the solidification process, and because the density of ilmenite is relatively high, crystals will sink to the bottom of the magma chamber in layers (Amethyst Galleries 2015). The titanium component of ilmenite does not weather as rapidly or completely as other minerals and is often left behind to form a major impurity in many silica sands worldwide. Ilmenite and its weathered products account for roughly 92% of all the titanium minerals consumed on an annual basis (Gribbin 2000).

Other Titanium Minerals of Interest

Virtually all titanium ore deposits are based on rutile, ilmenite, or one of the ilmenite alteration products. Other titanium minerals exist, and many have been explored for possible future use. This includes the titanium silicate sphene (also known as *titanite*, $CaTiSiO_5$), the rutile isomorph anatase, *perovskite* ($CaTiO_3$), and *eclogite* (Sandvik et al. 2010; Korneliussen et al. 2000). There are very large deposits of anatase in different regions of the world, for example, in Brazil; but none have been commercialized at scale because of the large amounts of ilmenite available and the presence of deleterious impurities such as calcium, phosphate, and radioactive elements (Stanaway 1994).

Economic Ores and Mining Processes

Two types of titanium mineral formations are being used commercially—rock and sand deposits—which are mined quite differently. The only rock ores mined in quantity are the Allard Lake deposit in Canada and Tellnes in Norway, both formed in anorthosite massifs as discussed in the literature (Morrisset 2008; Charlier et al. 2010). The other major mines are in mineral sands deposits, where rutile and primary and secondary ilmenite (along with other minerals) wash down from their region of exposure and mix with the dominant silica sand. Typically, these *heavy minerals* (defined as having a density greater than 2.9 kg/m^3) make up about 0.5% of the overall sand (Benjamin 2011). However, the action of waves and currents can lead to economic levels of heavy minerals, sometimes as high as 15%–30%, or even more. These ore deposits are found along many current or relict shorelines worldwide. Although mineral sands are much easier to mine than rock ores, they typically have higher costs of mineral processing, as the products more often go directly to the final product manufacturer, whereas the rock ores go into a smelting operation to increase their titanium content.

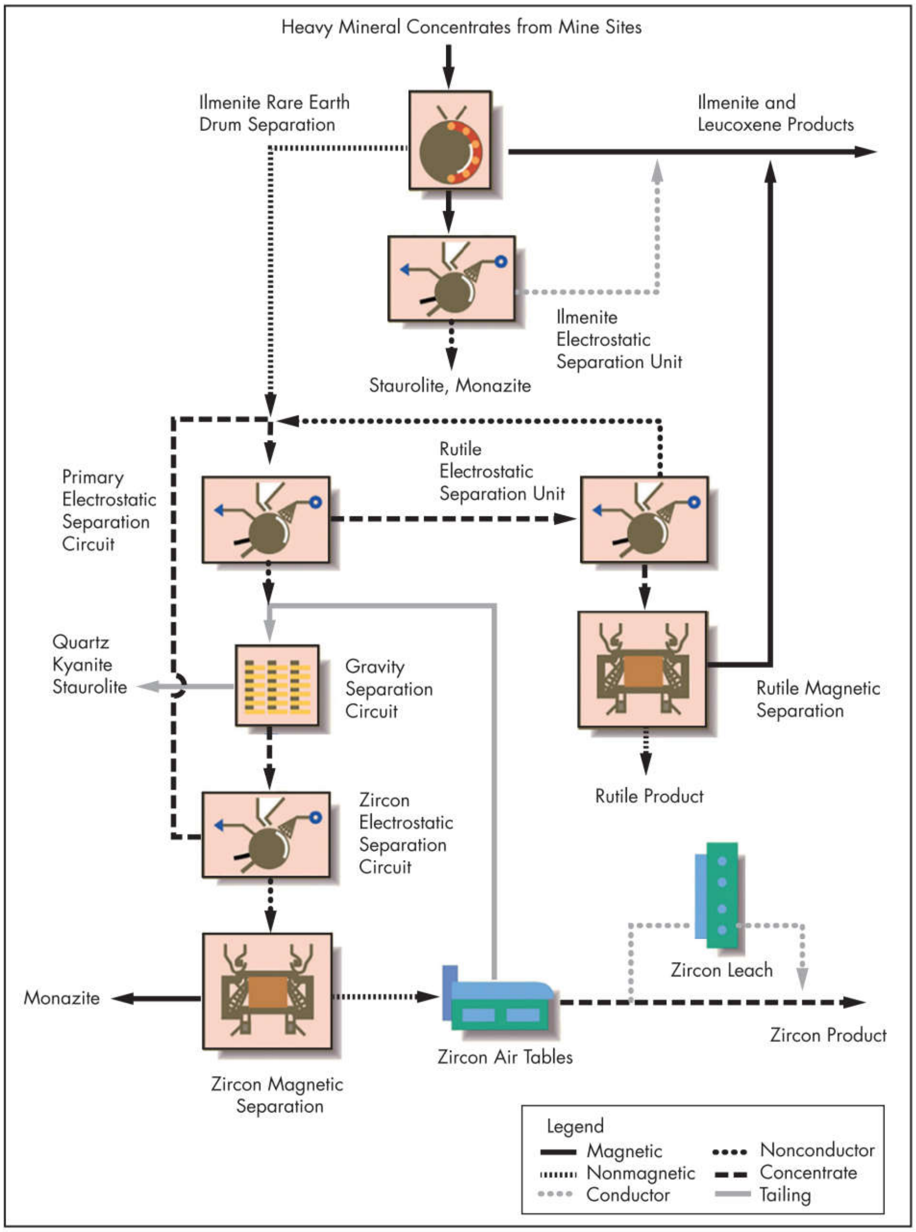
Rock Ores

For the huge open pit ilmenite mining operation in Quebec (Canada)—the Rio Tinto Fer et Titane (RTFT) Tio mine (also called the Allard Lake mine)—the ore is removed from the rock face by blasting, followed by crushing to –7.5 cm. The rock is then shipped to the smelter by train and ship (Rio Tinto, n.d.). Like other rock ores, the titanium content of the product after physical beneficiation is comparatively low (Table 2; Battle et al. 1993). No other rock ilmenite operation is nearly the size of Allard Lake. The only other deposit about which much is known is the Tellnes deposit in Norway (Korneliussen et al. 2000). Some rock ores are being mined in China (Hazen et al. 2008) and Russia (Makarov 2013).

Mineral Sands

The nature of mineral sands deposits lends itself to a unique form of mining. In wet dredging, the visible mining operation only affects a relatively small area at any given time, and it is difficult to visually detect that mining had taken place only a few years later. In this process, sand is taken up from a dune face using a scoop and fed to a wet concentrator (Minkler and Baroch 1981), typically containing spiral classifiers. This type of classifier can easily separate silica from heavier minerals. The silica is rejected into the pond behind the dredge, while the heavy mineral concentrate is taken ashore for further processing. Eventually the pond behind the dredge fills in, and the sand is planted in dune grasses (Geoscience Australia 2015). Dry dredging is also used in some mineral sands deposits where water is scarce or the characteristics of the mineral suite demand it (Jones 2009).

The details of a mineral separation plant (or dry mill) depends on the particular minerals in the heavy mineral suite, their characteristics in the specific locality, and the amount of those minerals that have some value in the open market. Generally at least two titanium minerals are separated (rutile and ilmenite), and a leucoxene product may be sold. Zircon is



Source: Jones 2009, reprinted with permission from the Australasian Institute of Mining and Metallurgy

Figure 1 Typical mineral sands dry mill

the most valuable coproduct and, at times, is more valuable than the titanium minerals. Some other minerals are also sold from mineral sands, including staurolite and foundry sands (Elsner 2010), but heavy mineral suites can also include garnet, tourmaline, epidote, monazite, xenotime, and aluminosilicates (Garnar 1972).

A typical dry mill flow sheet can be seen in Figure 1 (Jones 2009). Ilmenite can be separated from other heavy minerals (except magnetite) because it is slightly magnetic, whereas the other minerals are not. Rutile and zircon can be separated from each other by their differences in conductivity, with residual gangue removed by density differences (Williams and Steenkamp 2006). The dry mill at the new mineral sands mine in Georgia includes electrostatic and magnetic rollers, spirals, and shaker tables in its flow sheet. The result is four products: zircon, rutile, ilmenite, and leucoxene (Dunn et al. 2015).

TITANIUM ORES AND INTERMEDIATES

South Africa and Canada are the leading ilmenite-producing countries. Australia continues to produce the most rutile, with Sierra Leone not far behind.

Commercial Ores and Locations

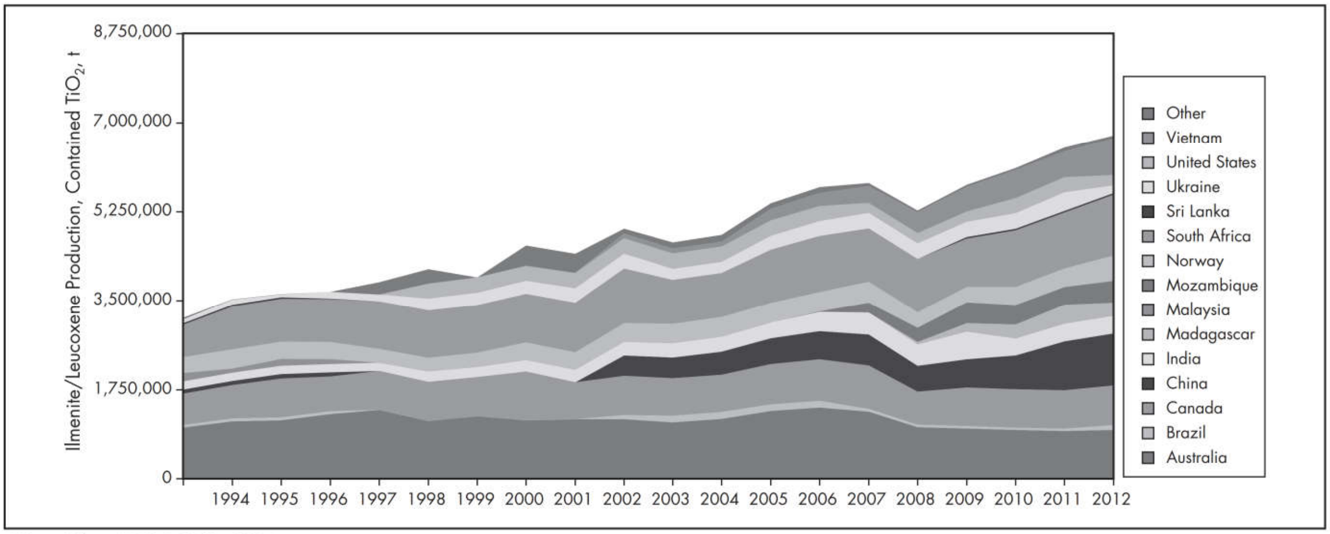
Table 3 shows the major individual titanium ore suppliers in 2013 (Bedinger 2018; Murty et al. 2007), while Figures 2 and 3 show the production of ilmenite/leucoxene and rutile, respectively, by country over the last 20 years (USGS 1993–2016). In that period, the amount of ilmenite and rutile mined by year has roughly doubled, with the amount of contained TiO_2 in

Table 3 Major titanium ore suppliers, 2013

Mine	Company	Country	Ore TiO_2 Concentration, %	Production of Contained TiO_2, t
Ilmenite				
Richards Bay Minerals (RBM)	Rio Tinto/BHP Billiton	South Africa	49	900,000
Rio Tinto Fer et Titane	Rio Tinto	Canada	35	770,000
Tellnes	TiZir	Norway	45	498,000
Moma Titanium Minerals Mine	Kenmare Resources	Mozambique	—*	430,000
Pangang	Pangang	China	48	384,000
Cooljarloo	Tronox	Australia	61	274,500
QIT Madagascar Minerals	Rio Tinto	Madagascar	—	264,000
Rutile				
Murray Basin	Iluka	Australia	—	170,000
Sierra Rutile	Iluka	Sierra Leone	96	125,000
Richards Bay Minerals	Rio Tinto/BHP Billiton	South Africa	—	100,000
Stradbroke Island	Sibelco/Unimin	Australia	—	70,000
Multiple	Group DF	Ukraine	—	60,000

Source: Bedinger 2018; Murty et al. 2007

*A dash indicates that the available references do not list the average TiO_2 content of the rutile or ilmenite mined.

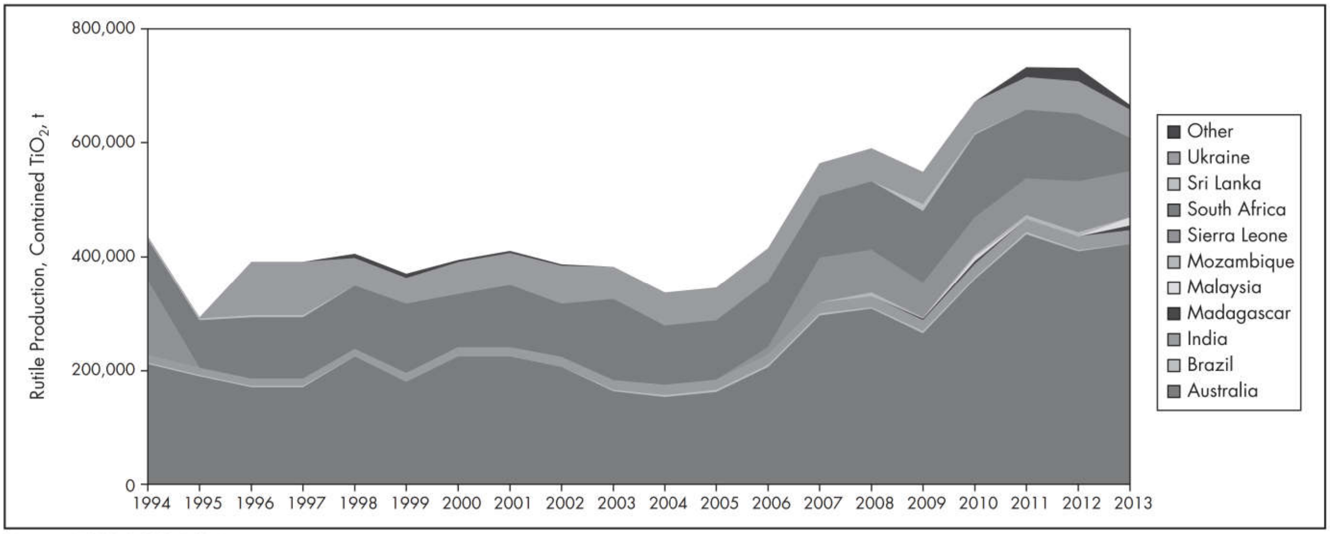


Adapted from USGS 1993–2016

Figure 2 Production of ilmenite and leucoxene by country

the mined ilmenite 9–10 times that of the rutile. Before further discussion, however, note that these numbers are not exact nor always self-consistent, for several reasons. The U.S. numbers are often not included because the U.S. Geological Survey (USGS) protects the confidentiality of individual companies. The numbers found in the literature were generally quoted as per metric ton contained TiO_2, but sometimes they are given as metric tons of ilmenite, without including the titanium content of the ilmenite. And sometimes, numbers are even given per metric ton of heavy mineral concentrate. Care must also be taken to minimize (or at least document) double counting those ores used to make slag or synthetic rutile.

In 1994, the dominant countries for ilmenite production were Australia, South Africa, Canada, and Norway. All four are currently among the leaders in production, but they have been joined by many other countries that were minor or nonexistent producers 20 years ago. In fact, of the four countries dominant in 1994, only South Africa has significantly increased the absolute amount of ilmenite produced over the last 20 years. Newer countries in the mix for ilmenite production are China, India, Ukraine, and Vietnam. In 2014, 69% of the ilmenite was produced by five countries: 18% in South Africa, 15% China, 14% Australia, and 11% each Canada and Vietnam. As for the companies involved in ilmenite production, the leaders are Rio Tinto and Iluka. Rio Tinto controls the former Quebec Iron and Titanium (QIT) property in Quebec, Canada (now called RTFT), and the Richards Bay Minerals (RBM) operation in South Africa, along with a new mine in Madagascar (the operation is called QIT Madagascar Minerals). Iluka owns or markets much of the ilmenite in Australia, along with a deposit in the United States. Norway is entirely represented by the Tellnes deposit, now owned by TiZir Limited. There are many newer individual producers, particularly in China, Ukraine, and Vietnam, along with India, which has always



Source: USGS 1993–2016

Figure 3 Production of rutile by country

supplied some level of ilmenite to the world market but was never one of the leading suppliers.

Overall year-to-year rutile production is much more variable, with production again approaching twice the level in 2013 as in 1994. Australia remains the dominant rutile supplier, and unlike the situation for ilmenite, its share has increased over time, from 49% to 63% of the total. South Africa has been steadily in second place, with lesser, but consistent amounts from Ukraine and India (the United States is not included in this figure). The major variable has been the production from Sierra Leone. It supplied 30% of world rutile in 1994, but from 1995 to 2005, Sierra Leone produced no rutile at all. The mine started up again in 2006 and supplied 12% of the world's rutile production in 2013. As for companies producing rutile, Iluka has the largest amount of the supply from Australia. The entire supply from Sierra Leone is the resurgent Sierra Rutile (now part of Iluka). Several different companies produce rutile in South Africa, India, and Ukraine.

Background and the Need for Chemical Beneficiation

The most economical titanium-containing feed to a production process is dependent on the final product to be made and the technology used to make that product. The vast majority of titanium ores are used to make titanium dioxide white pigment. TiO_2 is made by two methods. In the earlier technology development, the titanium minerals are dissolved in sulfuric acid, and later titanium is precipitated as a titanium oxysulfate, which is purified and converted to titanium dioxide. In the chloride process, the ore is reacted with coke and chlorine in a fluidized bed, and virtually all minerals are converted to gaseous chlorides. Titanium tetrachloride ($TiCl_4$) is then isolated from most other chlorides and further purified. To make TiO_2, pure $TiCl_4$ is reacted with oxygen at high temperatures, and the chlorine gas is recycled. In the major production process for titanium metal—the Kroll process—high-purity $TiCl_4$ is reacted with elemental magnesium to make titanium metal sponge and recyclable magnesium chloride.

Each of these production processes place their own demands on ore supplies. Both sulfate and chloride pigment processes are capable of using ilmenite directly, but not all ilmenite ores are suitable for both processes, hence the subcategories of *sulfatable* and *chlorinatable* ilmenite. In theory, ores used to make titanium metal could use chlorinatable ilmenite directly, but the plants are all so small that it is not considered economically viable to add the extra infrastructure to chlorinate, separate, and dispose of the non-titanium chlorides. Instead, their sources of titanium are natural rutile or artificial products made by chemical processing of ilmenite.

The three *natural* products (those made by mining and physical beneficiation only) are discussed first: sulfatable ilmenite, chlorinatable ilmenite, and natural rutile. The desirability of chemical beneficiation is then considered, along with the technologies that are being used to do the upgrading. Finally the entire suite of products available to a TiO_2 pigment manufacturer or titanium metal producer are summarized, along with expectations for the future.

Sulfatable Ilmenite

The most important characteristic of sulfatable ilmenite is that the ore is easily dissolved in sulfuric acid. This means that weathered ilmenite containing large amounts of ferric iron must be avoided, and tetravalent titanium is preferred over trivalent (McCoy et al. 2011). Impurities that do not dissolve in sulfuric acid, such as silica and zircon, can be easily separated from the titanium-rich solution, so that is not a limitation. However, the intermediate solid, titanium oxygen sulfate ($TiOSO_4$), is hard to purify, so several species that tend to follow titanium into solution (such as Cu, Ni, Mn, Cr, V, and Nb) should be avoided in the feed (McCoy et al. 2011). Ore size is not critical; the feed is generally ground to –45 µm.

Chlorinatable Ilmenite

Because the chloride process involves the use of a fluidized bed to react titanium ore with coke and chlorine, there are strict physical constraints on the ore feed size and density. The ore particles must be suspended in the stream of chlorine gas for long enough that the constituents of the ore can react with coke and chlorine to convert to gaseous chlorides or oxychlorides. Particles too large and dense cannot be supported by the gas stream and result in defluidization of the bed. Fine particles can elutriate from the bed before reactions are completed. At typical densities of ilmenite or rutile, the feed size needs to be in the range of 50 to 150 μm.

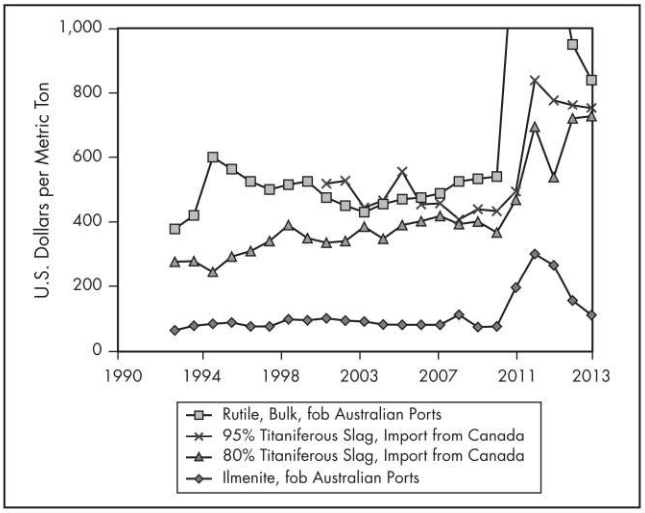
Chemically, the key issue for successful operation of the chloride-process fluidized bed is to avoid the production of significant quantities of liquids. The bed is designed for rapid conversion of fine solids to gases; liquid can lead to clumping of solids and defluidization of the bed. The main culprits at the temperatures and pressures of typical chloride-process operations are calcium, magnesium, and to a lesser extent, manganese. This greatly restricts use of some of the rock ilmenites that often contain significant concentrations of these impurities. Other impurities are mainly an issue because they raise or lower operating costs. The presence of trivalent titanium, rather than tetravalent, for example, reduces coke consumption. High levels of sulfur increase downstream gas-handling costs. Various impurities can be removed within the chloride process, such as Si, Zr, Nb, and V. This topic is discussed in more detail in Chapter 12.37, "Titanium Dioxide Pigment."

Natural Rutile

Natural rutile is a desirable feed for both titanium metal and pigment manufacture, because of the high TiO_2 and concomitantly low impurity content. However, there is not enough rutile to supply both customers, especially with the low cost of ilmenite relative to rutile. Ilmenite is inexpensive enough that it can be upgraded to various *synthetic* versions of rutile that can compete with the natural mineral in many applications.

Chemical Beneficiation of Ilmenite

Chemical analyses of eight natural ilmenites are given in Table 2. The titanium content of the different ilmenites can be compared to that of typical rutile TiO_2 contents of 90%–95%, and relative prices in Figure 4, which represents the period from 1992 to 2015 (Elsner 2010; USGS 1993–2016). The cost of ilmenite is roughly a fifth that of rutile, but of course, the value-in-use is much less as well, as the end user must now cope with increasing quantities of iron and possibly other impurities as well. Given the lack of enough natural rutile to supply all downstream needs, the possibility of chemically upgrading ilmenite to make a higher TiO_2 product is appealing both for the customer and for certain suppliers, especially those possessing ilmenite deposits of very low grade. The main question is whether this upgrading can be accomplished while keeping product cost competitive with that of rutile.



Source: Elsner 2010; USGS 1993–2016

Figure 4 Ilmenite, rutile, and slag prices, 1992–2013

In the 1940s, a huge deposit of rock ilmenite was discovered in Quebec, not far inland from the St. Lawrence River near Allard Lake. However, the percentage of titanium obtainable by standard physical beneficiation was too low for any application at the time. A technology was needed to upgrade the titanium content to an acceptable level, while ideally getting value for the iron impurity. The technology developed was carbothermic reduction in an electric arc furnace at elevated temperature. Under these conditions, the carbon in the feed preferentially reacts with the iron component of the ore to make metallic iron. Because metallic iron is much heavier than the slag phase that contains the titanium, the iron sinks to the bottom of the reaction vessel and is easily separated from the enriched titanium above. The process was successfully implemented in Sorel, Quebec, in the mid-1950s, and Sorelslag has been part of the titanium feedstock equation ever since (Habashi 1986, 2010).

Since that time, many other ilmenite smelting plants have been developed, all producing a high-TiO_2 slag product. Because of the high operating costs and operational difficulties with the smelting process, many other ilmenite upgrading technologies have been developed (Battle et al. 1993). Most successful have been the solid-state reduction technologies that produce synthetic rutile, and many of these plants are currently operating, mainly in Australia and India. Smelting and commercial synthetic rutile manufacturing technologies and practitioners are discussed in the following section, with a brief consideration of upgrading technologies not yet commercialized.

Ilmenite Smelting

Not every low-grade titanium feedstock can be used to make a high-quality titania slag: The chemical composition must be within a particular range. Ilmenite smelting does not separate all of the impurities from the titanium fraction of an ilmenite ore. It removes most of the iron, indeed, but removal of other impurities depends on system temperature and pressure, and the thermodynamics and kinetics of elemental partitioning between molten iron and the liquid slag phase dominated by titanium oxides. Those considering ilmenite smelting of a particular ore must consider the actual partitioning of elements in slag versus metal, and they must determine if any particular component is likely to exceed desired limits in either the slag product or the metallic iron.

If modeling and experiments indicate that the predicted slag is likely to have an unfavorable composition, decisions will be necessary to continue the project. Changes could include the following:

- Use a different ore source or blend.
- Modify the ore before it reaches the smelter.
- Modify the operating conditions of the smelter to optimize operation with that particular feed.
- Modify the product slag after it is created.
- Live with the reduced value of a product with excessive levels of one or more impurities.

All of these options have been explored at one time or another by smelter operators.

For example, it was realized early in the development of the RBM smelting operation that the ores of choice were relatively high in chromium, which would produce a slag with chromium oxide levels unacceptable to customers. Their solution was to subject the concentrate to an oxidizing roast, which converts the ilmenite fraction of the ore to a more magnetic state allowing for separation from the high-Cr minerals (Steenkamp et al. 2005). The same approach does not necessarily work on all ilmenites; in Australia, a sulfidizing pretreatment might be more appropriate (Ahmad et al. 2015).

Although carbothermic reduction of metal oxides is a well-established technology, there are certain unique features making ilmenite processing more difficult than for most other metal oxides. One problem is that the slag product is actually more valuable than the iron. In normal metal smelting, the slag has the critical role of absorbing impurities that would otherwise enter the valuable metal phase and helps to control heat transfer, the liquid state of the system, and its flow properties. Often, fluxes are added to the slag to lower its melting point and make operations safer and lower cost. That cannot be done here, as any additions to the slag would dilute product quality. Thus, ilmenite smelters must operate at temperatures in excess of 1,750°C for the high-TiO_2 slag to have the right fluidity for feed materials to rapidly fall through the slag to the metal phase and for adequate product flow exiting the system when tapped.

Another problem is that no one has yet found a refractory material for lining smelters at these temperatures that can hold up to the corrosive and erosive effects of high titania slags. The ingenious solution has been to water-cool the outer shell of the reactor such that a layer of slag freezes against the inner shell, thus protecting the refractory from further attack. The downside of this is that tight thermal control of the reactor is required to keep this frozen shell intact.

It is also not economically realistic to remove all of the iron oxide from the slag; typical operations lead to a slag containing roughly 10% FeO. This happens because as the iron content of the slag is reduced, its activity decreases while that of the titanium increases. At a certain time, therefore, the reducing agent acts to reduce tetravalent titanium to trivalent, with less and less of the carbon being used to reduce ferrous to metallic iron. The increased value of slightly more pure slag is generally outweighed by the extra energy costs to get to the lower iron (Burger et al. 2009); in addition, not all customers are happy to get a slag with high Ti_2O_3 content as opposed to TiO_2.

The original ilmenite smelting operation in Quebec now has nine smelting furnaces, all more than 40 years old, but modernized over time. The technology was transferred to Rio Tinto's RBM operation in South Africa, which makes similar production levels from "... four of the world's largest six-in-line electric arc furnaces. The furnaces are rectangular in shape, being 18 metres long and eight metres wide, and have six electrodes in line" (Williams and Steenkamp 2006). Although there are several other ilmenite smelting operations now in operation around the world, none approach the size of the two Rio Tinto operations.

The quality of the titania slag is directly related to the quality of the ore feed. This is quite obvious with a comparison between Sorelslag and the slag created using the sands from Richards Bay. Because the rock ilmenite contains much higher levels of impurities (particularly MgO) that tend to stay in the slag and not be reduced, the final TiO_2 content of rock-ilmenite slag is considerably lower than Richards Bay slag. And it gets worse, because the impurities accentuated in the Sorelslag are the most problematic impurities for the operation of the chloride process to make TiO_2 or the Kroll process to make titanium metal. At the temperatures of operation of the fluid-bed chlorinator in these processes, both magnesium chloride and calcium chloride are liquid, which can lead to severe operating problems if not carefully controlled and monitored. No chloride operation can operate on high percentages of Sorelslag. This became a particular problem in the 1990s as the number and size of chloride plants increased (Rio Tinto, n.d.). Rio Tinto's solution was to develop new technology to remove impurities from the Sorelslag to make an upgraded slag (UGS). This process involves oxidation of the slag to convert all reduced titania to insoluble TiO_2, followed by reduction to convert all iron to ferrous, then an acid leach to dissolve the iron and other impurities, leading to a product containing 94.5% TiO_2, suitable for all titanium applications. Since that time, Rio Tinto has marketed Sorelslag to sulfate pigment producers and UGS to others. Most recently, they have begun making higher quality slag by another route, which is shipping high-grade ilmenite from QIT Madagascar Minerals to the smelters in Quebec.

Known smelting operations are listed in Table 4 (Elsner 2010). Prominent are the multiple-smelter operations of Rio Tinto in Quebec, Canada, and Richards Bay, South Africa. In the last 20 years, two smaller operations have started up in South Africa—Namakwa Sands and KZN Sands. The Tinfos smelter in Norway began operation in 1986 and soon encountered the same problems as Rio Tinto, as their local rock ilmenite led to slags that could be sold only to sulfate pigment producers. They were the first to try and make a high-grade slag by importing higher-grade ilmenite, but the initiative did not last long (Gambogi 1997, 1999). Now it appears they will try that approach again, this time with a new high-quality ilmenite sand from Senegal (Bedinger 2015).

Little is known about the other slag producers listed in Table 4, other than their existence. There is one article summarizing titanium slag production in Russia and Kazakhstan (Toembaeva 2015).

Hydrometallurgical Upgrading

Even with the success of the smelting operation in Quebec, it was not obvious to other ilmenite producers that this was the technology to emulate for upgrading their own ores. Operation, particularly in the early years, was very tricky (Rio Tinto, n.d.). Also, energy costs are inherently very high, with significant capital costs required for the smelter and attendant equipment. In Australia in the 1960s, a much lower-cost technology was developed—the Becher process, or as it is sometimes known, the Lurgi–Becher process.

The flow sheet for the Becher process can be seen in Figure 5 (Iluka 2012). The ore is pre-oxidized, if necessary, then reduced in a rotary kiln in the solid state to make metallic iron. After magnetic separation of the reduced ilmenite from char and ash, it is leached for several hours in an aerated aqueous solution that contains ammonium chloride as a catalyst (Battle et al. 1993). The iron is converted to oxides that can be washed off the TiO_2, resulting in what became known as *synthetic rutile* (SR). This process has low capital and operating costs but does not result in complete removal of the iron,

Table 4 High-TiO_2 slag producers

Company	Location	Initial Operation	Number and Type of Furnaces*	Overall Capacity, t/yr slag	TiO_2 Content of Ore, %	TiO2 Content of Slag, %
Rio Tinto	Quebec, Canada	1950	9 AC	1,000,000	34	80
Rio Tinto	Richards Bay, South Africa	1977	4 AC	1,000,000	50	85
TiZir	Tyssedal, Norway	1986	1 AC	200,000	44	80
Tronox	Namakwa Sands, South Africa	1995	2 DC	200,000	52	86
Tronox	KZN Sands, South Africa	2003	2 DC	250,000	47	85
Pangang	Pangang, China	2006	Unknown	100,000	48	Unknown
Various	Vietnam	2010–2014	5	64,000	Unknown	Unknown
Xinli	Kunming, China	2009	DC	80,000	Unknown	80–90

Source: Elsner 2010
*AC = alternating current; DC = direct current.

and the iron removed must be disposed of, rather than being a valuable coproduct as in smelting. Besides reducing the iron content of the feed, manganese can be removed by adding sulfur to the reduction kiln, then acid washing the manganese sulfide from the product; something similar might be done to remove chromium residues as well (Ahmad et al. 2015).

Commercial Becher operations are listed in Table 5. All operations are located in Western Australia, operated by either Iluka or Tronox. Tronox markets half of their SR and uses the remainder in their pigment plant in Kwinana. Iluka makes several different products in their SR plants: basic SR; premium SR (removal of Mn and some Fe as sulfides, mentioned earlier); synthetic rutile enhanced product, which uses a complicated flow sheet specifically to lower the thorium and uranium contents of the ore; and a low-grade SR85, made from their Murray Basin ilmenite (Iluka 2012).

No other SR process has been as successful as the Becher process. The only other technology known to have multiple plants is the Benelite process, where reduced ilmenite is leached in 20% HCl at elevated temperatures and pressures. This can be followed by acid regeneration to reform the HCl. The Wah Chang process is similar but uses stronger acid (Battle et al. 1993). Plants using these technologies have predominantly been built in India (Indian Bureau of Mines 2015) and are also listed in Table 5.

The Ishihara process used the waste sulfuric acid from the company's sulfate-route pigment plant in Japan. The acid was used to leach ilmenite after partial reduction of the iron. Colloidal hydrated TiO_2 was used in the leaching step as a reaction accelerator. The waste acid was used in the production of ammonium sulfate. The original ore particle size was retained during processing (Battle et al. 1993). This process was only used by Ishihara in its Osaka facility; the plant was shut down in 1994.

Other Ilmenite Upgrading Technologies

Research continues to improve or replace current ilmenite upgrading technologies; many of these were summarized 20 years ago (Battle et al. 1993). Only a few more recent technologies can be summarized here.

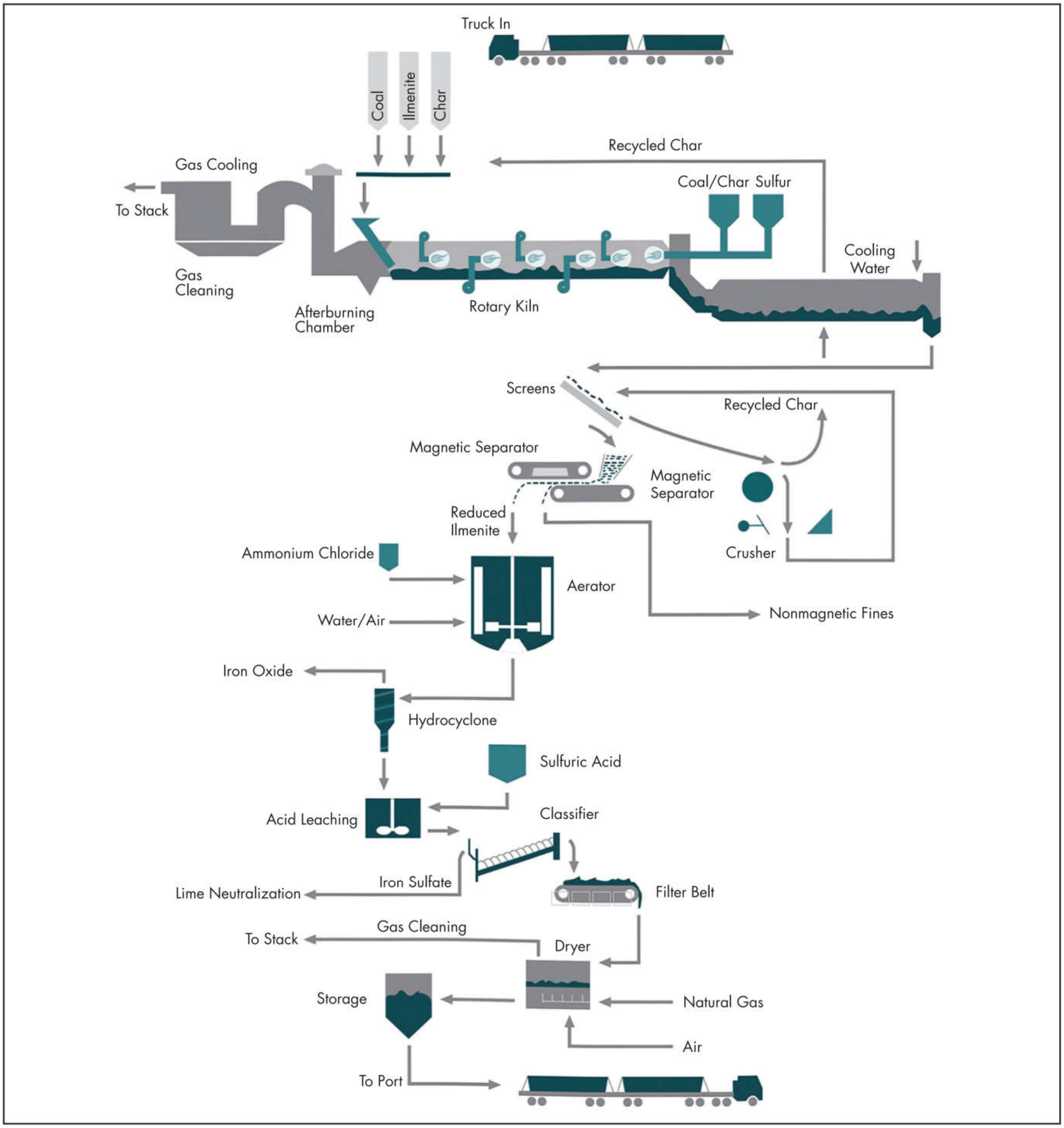
One of the major goals has been to unite the great advantages of the smelting and SR routes—to run low-temperature, relatively simple, energy-saving unit operations—yet achieve a high removal percentage of iron and create a valuable iron coproduct. The world's largest single consumer of titanium raw materials, DuPont (recently separated from the parent company as part of Chemours) has made several attempts at this type of technology improvement over the years (Battle et al. 1996; Shekiro et al. 2011).

Quite a number of newer technologies are focused on upgrading Ti-rich slags to make the product more saleable (in the case of some, converting a slag of little or no value to high value). More than 20 years ago, six options were identified, as given in the following list (Battle et al. 1993). Modern-day flow sheets still seem to fit into this list, with perhaps the acid changed in leaching operations, use of new power sources such as microwaves, or additional unit operations included (Guo et al. 2011; Qian et al. 2011; Lakshmanan et al. 2011; Mehdilo and Irannajad 2012; Nell 2007; Abdou et al. 2005; Lei et al. 2011):

1. **Extended reduction.** The iron content is reduced to 1%–2%. Much of the Si, Mn, Cr, and V is removed. Essentially, all of the titanium is reduced to the +3 valence state.
2. **Selective chlorination.** Residual Fe, as well as Cr, V, and some Mg are removed.
3. **Sulfidation and acid leach.** Fe, Cr, and V are removed.
4. **Sulfation roast and leaching.** Mg and Ca are converted to soluble sulfates. Iron must be removed first, perhaps by Na_2S. Silica is also removed.
5. **Reduction of Ti to Ti(O,C).** This species chlorinates at low temperatures, before remaining impurities.
6. **Absorption of impurities in coke.** The *Scoke* process creates micropellets from slag and coke. The liquid chlorides soak into residual coke, which may prevent the fluidization problems that they would otherwise cause.

Iluka is working on developing acid-soluble SR, to open the market for this product to sulfate pigment producers (Iluka 2012). Other concepts include separating different Ti-containing phases in low-grade ilmenite ores by magnetic separation, then treating the two streams separately to optimize titanium separation and yield (Jha et al. 2011) and using microwave energy to reduce costs (Shaohua et al. 2012).

Technologies are also being developed to support downstream technological innovations in the titanium field, for example, modifying the Becher process to make titanium oxycarbide instead of titanium dioxide, to be used as the feed to an electrochemical process to make titanium metal (Fatollahi-Fard and Pistorius 2015).



Source: Iluka 2012

Figure 5 Flow sheet for the improved Becher synthetic rutile process

TITANIUM-RICH FEEDSTOCKS FOR TITANIUM DIOXIDE AND TITANIUM METAL PRODUCTION

In previous sections, the titanium minerals processing business has been discussed, from the prevalence of ilmenite over rutile to the desire by customers for feeds at ilmenite prices but the purity of rutile. The result is a plethora of products available for use by the TiO_2-pigment and Ti-metal industries. These products are listed in Table 6 (Iluka 2014; Nell 2007; USGS 1993–2016), along with approximate amounts produced in 1990 and 2006, and prices.

Overall production of titanium feedstocks has increased appreciably over the past 20 years, although not across the board. High-grade feeds have increased (particularly those for the chloride process) at the expense of lower-grade and sulfate feedstocks.

Any snapshot of pricing, especially in the environment of the past several years, should be examined with caution.

Table 5 Commercial synthetic rutile production

Company	Location	Capacity, t/yr	Ilmenite TiO_2 Content, %	SR TiO_2 Content, %
Becher Process				
Iluka		500–550,000	—[*]	—
	Capel, Australia	—	—	—
	Narngulu, Australia	—	—	—
Tronox	Chandala, Australia	220,000	61	92
Benelite Process				
Indian Rare Earths Limited (Orissa Sands Complex)	Chatrapur, India	100,000[†]	50	91
Kerala Minerals and Metals Limited	Chavara, India	50,000	60	93
Cochin Minerals and Rutile Limited	Kerala, India	45,000	—	—
Tor Minerals	Ipoh, Malaysia	—	—	—
Kerr-McGee	Alabama, United States	Operated 1976–2003[†]		
Wah Chang Process				
DCW	Sahupuram, India	48,000	—	95
Ishihara Process				
Ishihara	Ishihara, Japan	Operated 1971–1994[†]		

[*] A dash indicates that the available references do not list the average TiO_2 content of the rutile or ilmenite mined.

[†] Not operating.

Table 6 Titanium feedstocks

Feedstock[*]	TiO_2 Content, %	Total Production of Contained TiO_2 in 1990, t	Total Production of Contained TiO_2 in 2006, t	Price in 2013, $/t
Natural rutile	95–97	492,000	390,000	1,250
Synthetic rutile	88–95	397,000	810,000	1,150
Upgraded slag	95	0	170,000	No information
Chloride slag	85–90	531,000	990,000	777
Sulfate slag	80–85	1,050,000	780,000	538
Chloride ilmenite	58–62	487,000	470,000	No information
Sulfate ilmenite	52–54	1,205,000	890,000	265

Source: Iluka 2014; Nell 2007; USGS 1993–2016

[*] These feedstocks are used to produce TiO_2 pigment and Ti metal.

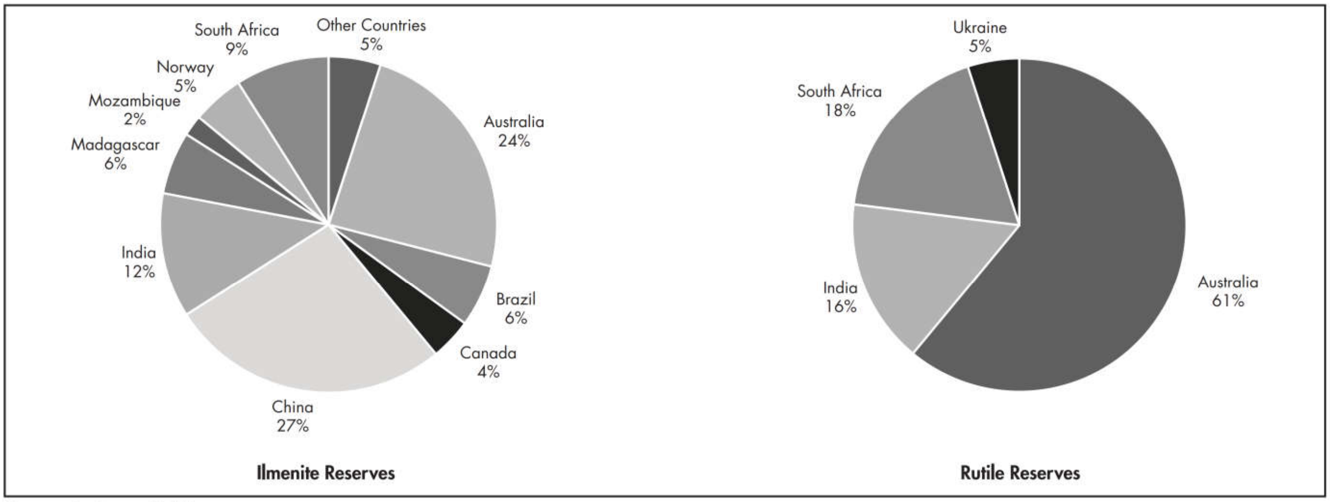
From 1992 to 2015 (Elsner 2010; USGS 1996–2016), ilmenite prices were steady at just less than US$100/t, whereas rutile prices increased from US$400/t to $500/t and became steady at that level. This compares with numbers quoted at US$60–$80 for ilmenite in India in 2006, SR at US$360–$440, and slag at US$370–$410 (Murty et al. 2007). Prices skyrocketed in 2010, however, and have only just begun to settle down. According to the USGS (Bedinger 2018), this was caused by a shortage of concentrate, or more picturesquely, "shortages in 2010 and 2011 led to a price spike and super profits before both collapsed under a mountain of inventories in 2012" (Barlow 2015). The feedstock market is improving, although the market has to adjust to China moving from a large importer of ilmenite to a country exporting low-cost ilmenite that is a by-product of iron ore mining: "Current factory gate prices of around US$100 are a symptom of the massive stockpiles that have accrued" (Barlow 2015).

In their detailed discussion of mineral sands pricing, Iluka describes former "constrained pricing" because of long-term contracts (Iluka 2014). Iluka ended legacy contracts in 2010, and now contracts are renegotiated quarterly or half yearly, with some spot sales.

The overall changes in the market in the past few years are summarized by Barlow (2015):

> Titanium dioxide is never more than two or three feet away from you at any given time. The ubiquity of its application means that global demand trends run closely with gross world economic product. This should mean that producers can rely on a fairly predictable set of metrics by which to forecast their market. However, the last 10 years have been anything but predictable. We have witnessed the departure of synchronicity between feedstock mining and pigment production, exacerbated by the global financial crisis and the explosion of Chinese capacity, which saw that country turn from a key net importer to an exporting behemoth in a few short years.

Both titanium dioxide and titanium metal markets are expected to continue to grow in upcoming years. There are few cost-effective alternatives to titanium dioxide in many of its applications, and titanium metal's unique combination of physical and chemical properties will make it more popular, particularly if the price of the finished product can be lowered. So there will be demand for more titanium ore, although new ores will need to meet ever more stringent demands in product quality and environmental responsibility. Fortunately, titanium ores, particularly ilmenites, are in great supply and



Source: Bedinger 2015

Figure 6 Current world reserves of titanium minerals

should not run out anytime soon. As shown in the pie charts of Figure 6 (Bedinger 2015), there are roughly 720 Mt (million metric tons) of ilmenite reserves (more than a 100-year supply for all titanium units needed) and 47 Mt of rutile and leucoxene (over a 50-year supply). This likely does not include the great supply of titanium in the titaniferous ores that are currently being mined almost exclusively for their iron content. Work continues on ways to economically use the titanium content of these ores (Taylor et al. 2006).

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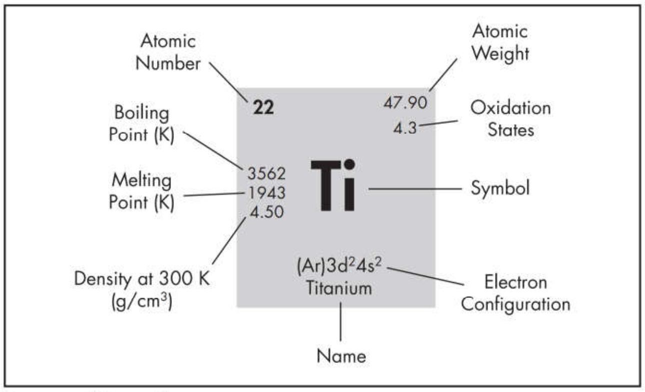
CHAPTER 12.39

Titanium and Titanium Alloys

M. Ashraf Imam and Francis H. (Sam) Froes

The characteristics of titanium are shown in Figure 1. The conventional processing of titanium metal occurs in four major steps: reduction of titanium ore into *sponge*, a porous form; melting of sponge, or sponge plus a master alloy, to form an ingot; primary fabrication, where an ingot is converted into general mill products, such as a billet, bar, plate, sheet, strip, and tube; and secondary fabrication of finished shapes from mill products. An alternate fabrication route is by powder metallurgy (including additive manufacturing), which can have economic advantages compared to the conventional processing route.

Titanium has high passivity; therefore, it exhibits high levels of corrosion resistance to most mineral acids and chlorides. It is also nontoxic and biologically compatible with human tissue and bone, making it an ideal material for medical implant products (Housley 2007; Imam et al. 2010; Froes et al. 1985).



Courtesy of Rector-Elements

Figure 1 Characteristics of titanium

USES

Titanium is used extensively in aerospace applications (both engines and airframes). It is also commonly used in implant components, automobiles (particularly in rotating and reciprocating parts of the internal combustion engine), the oil and gas industries, chemical processing equipment, sporting equipment, and consumer products.

HISTORICAL PRICE

The historical price of titanium sponge is shown in Figure 2. As this sponge is melted to form an ingot and subsequently fabricated to various mill products, the price increases, which is shown in Figure 3.

OCCURRENCE

Titanium occurs in nature in many forms, most notably as ilmenite ($FeTiO_3$) and rutile (tetragonal TiO_2). In the production of titanium metal, only high-grade titanium ores are utilized, such as natural rutile, ilmenite processed to make synthetic rutile, or high-TiO_2 slags. Titanium ores and their processing are discussed in another chapter of this handbook.

PROPERTIES

Titanium alloys may be divided into two principal categories: corrosion-resistant and structural (Housley 2007; Imam et al. 2010; Froes et al. 1985). The corrosion-resistant alloys are generally based on a single-phase (alpha) microstructure with dilute additions of solid solution strengthening and alpha-stabilizing elements, such as oxygen (interstitial), palladium, ruthenium, and aluminum (substitutional). These alloys are used in the chemical, energy, paper, and food processing industries to produce highly corrosion-resistant tubing, heat exchangers, valve housings, and containers. The single-phase alpha alloys provide excellent corrosion resistance, good weldability, and easy processing and fabrication, but a relatively low strength.

In markets served by major U.S. titanium producers, corrosion-resistant alloys comprise approximately 25% of the total output; Ti-6Al-4V, 60%; and all other structural alloys, the remaining 15%.

MANUFACTURING

The commercial production of titanium metal, by the Kroll process (Figure 4), involves the chlorination of rutile (TiO_2)

M. Ashraf Imam, Faculty/Research Professor, George Washington University, Washington, D.C., USA
Francis H. (Sam) Froes, Consultant, Tacoma, Washington, USA