

Smelting and Refining of Cu, Pb, Zn, Ti and Ni

In the production and refining of metals, valuable components are separated from worthless material in a series of different physical and chemical reactions. The end-product is metal containing controlled amounts of impurities. Primary smelting and refining produce metals directly from ore concentrates, while secondary smelting and refining produces metals from scrap and process waste. Scrap includes bits and pieces of metal parts, bars, turnings, sheets and wire that are off-specification or worn-out but are capable of being recycled

Overview of Processes

Two metal recovery technologies are generally used to produce refined metals, *pyrometallurgical* and *hydrometallurgical*. Pyrometallurgical processes use heat to separate desired metals from other materials. These processes use differences between oxidation potentials, melting points, vapour pressures, densities and/or miscibility of the ore components when melted.

Hydrometallurgical technologies differ from pyrometallurgical processes in that the desired metals are separated from other materials using techniques that capitalize on differences between constituent solubilities and/or electrochemical properties in aqueous solutions.

Pyrometallurgy

During pyrometallic processing, an ore, after being *beneficiated* (concentrated by crushing, grinding, floating and drying), is sintered or roasted (calcined) with other materials such as baghouse dust and flux. The concentrate is then smelted, or melted, in a blast furnace in order to fuse the desired metals into an impure molten bullion. This bullion then undergoes a third pyrometallic process to refine the metal to the desired level of purity. Each time the ore or bullion is heated, waste materials are created. Dust from ventilation and process gases may be captured in a baghouse and are either disposed of or returned to the process, depending upon the residual metal content. Sulphur in the gas is also captured, and when concentrations are above 4% it can be turned into sulphuric acid. Depending upon the origin of the ore and its residual metals content, various metals such as gold and silver may also be produced as by-products.

Roasting is an important pyrometallurgical process. Sulphating roasting is used in the production of cobalt and zinc. Its purpose is to separate the metals so that they can be transformed into a water-soluble form for further hydrometallurgical processing. The smelting of sulphidic ores produces a partially oxidized metal concentrate (matte). In smelting, the worthless material, usually iron, forms a slag with fluxing material and is converted into the oxide. The valuable metals acquire the metallic form at the converting stage, which takes place in converting furnaces. This method is used in copper and nickel production. Iron, ferrochromium, lead, magnesium and ferrous compounds are produced by reduction of the ore with charcoal and a flux (limestone), the smelting process usually taking place in an electric furnace.

The high temperature required for the pyrometallurgical treatment of metals is obtained by burning fossil fuels or by using the exothermic reaction of the ore itself (e.g., in the flash smelting process).

The flash smelting process is an example of an energy-saving pyrometallurgical process in which iron and sulphur of the ore concentrate are oxidized. The exothermic reaction coupled with a heat recovery system saves a lot of energy for smelting. The high sulphur recovery of the process is also beneficial for environmental protection. Most of the recently built copper and nickel smelters use this process.

Hydrometallurgy

Hydrometallurgical processes includes leaching, precipitation, electrolytic reduction, ion exchange, membrane separation and solvent extraction. The first stage of hydrometallurgical processes is the leaching of valuable metals from less valuable material, for example, with sulphuric acid. Leaching is often preceded by pre-treatment (e.g., sulphating roasting). The leaching process often requires high pressure, the addition of oxygen or high temperatures. Leaching may also be carried out with electricity. From the leaching solution the desired metal or its compound is recovered by precipitation or reduction using different methods.

Electrolysis of metals in aqueous solutions is also considered to be a hydrometallurgical process. In the process of electrolysis the metallic ion is reduced to the metal. The metal is in a weak acid solution from which it precipitates on cathodes under the influence of an electrical current. Most non-ferrous metals can also be refined by electrolysis.

Often metallurgical processes are a combination of pyro- and hydrometallurgical processes, depending on the ore concentrate to be treated and the type of metal to be refined. An example is nickel production.

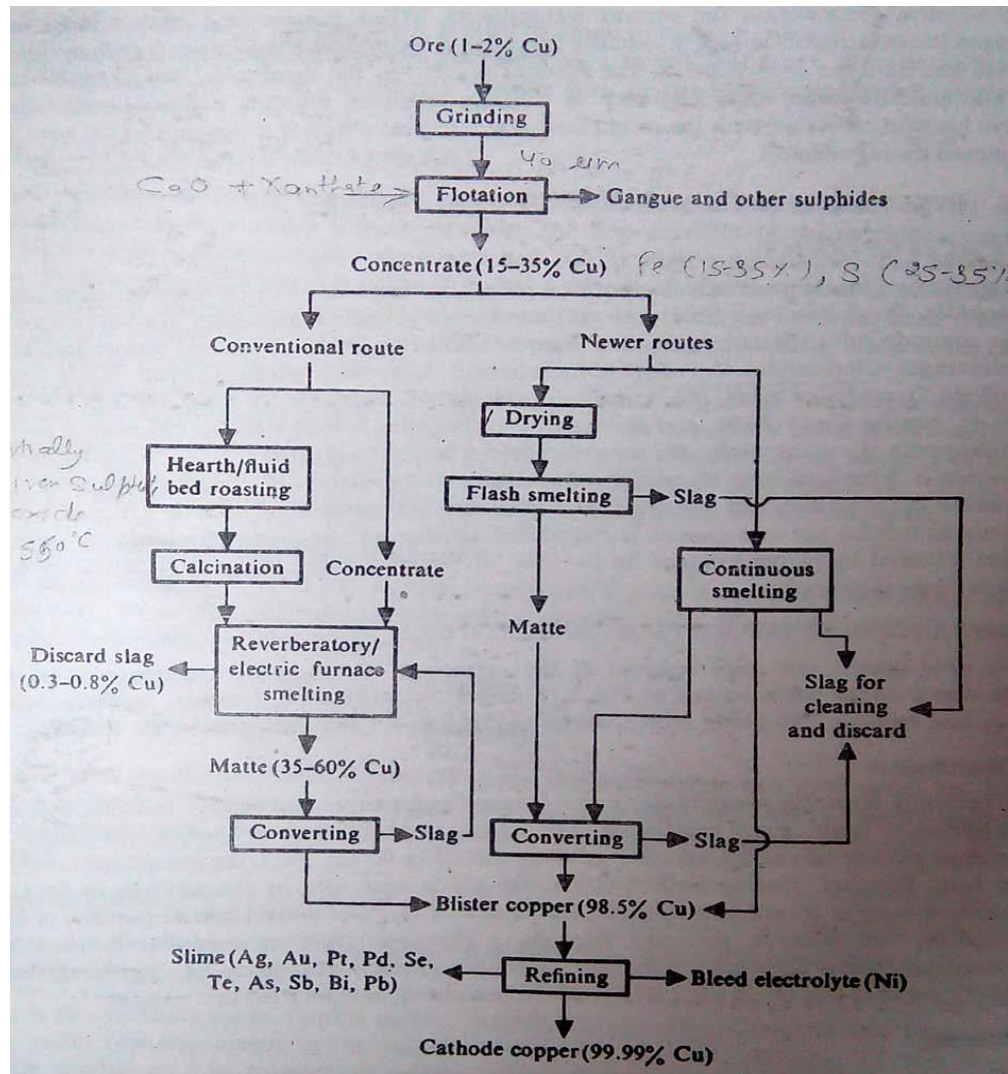
Copper

Copper is mined in both open pits and underground mines, depending upon the ore grade and the nature of the ore deposit. Copper ore typically contains less than 1% copper in the form of sulphide minerals. Once the ore is delivered above the ground, it is crushed and ground to a powdery fineness and then concentrated for further processing. In the concentration process, ground ore is slurried with water, chemical reagents are added, and air is blown through the slurry. The air bubbles attach themselves to the copper minerals and are then skimmed off the top of the flotation cells. The concentrate contains between 20 and 30% copper. The tailings, or gangue minerals, from the ore fall to the bottom of the cells and are removed, dewatered by thickeners and transported as a slurry to a tailings pond for disposal. All water used in this operation, from dewatering thickeners and the tailings pond, is recovered and recycled back into the process.

Copper can be produced either pyrometallurgically or hydrometallurgically depending upon the ore-type used as a charge. The ore concentrates, which contain copper sulphide and iron sulphide minerals, are treated by pyrometallurgical processes to yield high purity copper products. Oxide ores, which contain copper oxide minerals that may occur in other parts of the mine, together with other oxidized waste materials, are treated by hydrometallurgical processes to yield high purity copper products.

Copper conversion from the ore to metal is accomplished by smelting. During smelting the concentrates are dried and fed into one of several different types of furnaces. There the sulphide

minerals are partially oxidized and melted to yield a layer of matte, a mixed copper-iron sulphide and slag, an upper layer of waste.



The matte is further processed by converting. The slag is tapped from the furnace and stored or discarded in slag piles onsite. A small amount of slag is sold for railroad ballast and for sand blasting grit. A third product of the smelting process is sulphur dioxide, a gas which is collected, purified and made into sulphuric acid for sale or for use in hydrometallurgical leaching operations.

Following smelting, the copper matte is fed into a converter. During this process the copper matte is poured into a horizontal cylindrical vessel (approximately 10m x 4m) fitted with a row of pipes. The pipes, known as tuyères, project into the cylinder and are used to introduce air into the converter. Lime and silica are added to the copper matte to react with the iron oxide produced in the process to form slag. Scrap copper may also be added to the converter. The furnace is rotated so that the tuyères are submerged, and air is blown into the molten matte causing the remainder of the iron sulphide to react with oxygen to form iron oxide and sulphur dioxide. Then the converter is rotated to pour off the iron silicate slag.

Once all of the iron is removed, the converter is rotated back and given a second blow of air during which the remainder of the sulphur is oxidized and removed from the copper sulphide. The converter is then rotated to pour off the molten copper, which at this point is called blister copper (so named because if allowed to solidify at this point, it will have a bumpy surface due to the presence of gaseous oxygen and sulphur). Sulphur dioxide from the converters is collected and fed into the gas purification system together with that from the smelting furnace and made into sulphuric acid. Due to its residual copper content, slag is recycled back to the smelting furnace.

Blister copper, containing a minimum of 98.5% copper, is refined to high purity copper in two steps. The first step is fire refining, in which the molten blister copper is poured into a cylindrical furnace, similar in appearance to a converter, where first air and then natural gas or propane are blown through the melt to remove the last of the sulphur and any residual oxygen from the copper. The molten copper is then poured into a casting wheel to form anodes pure enough for electrorefining.

In electrorefining, the copper anodes are loaded into electrolytic cells and interspaced with copper starting sheets, or cathodes, in a bath of copper sulphate solution. When a direct current is passed through the cell the copper is dissolved from the anode, transported through the electrolyte and re-deposited on the cathode starting sheets. When the cathodes have built-up to sufficient thickness they are removed from the electrolytic cell and a new set of starting sheets is put in their place. Solid impurities in the anodes fall to the bottom of the cell as a sludge where they are ultimately collected and processed for the recovery of precious metals such as gold and silver. This material is known as anode slime.

The cathodes removed from the electrolytic cell are the primary product of the copper producer and contain 99.99+% copper. These may be sold to wire-rod mills as cathodes or processed further to a product called rod. In manufacturing rod, cathodes are melted in a shaft furnace and the molten copper is poured onto a casting wheel to form a bar suitable for rolling into a 3/8 inch diameter continuous rod. This rod product is shipped to wire mills where it is extruded into various sizes of copper wire.

In the hydrometallurgical process, the oxidized ores and waste materials are leached with sulphuric acid from the smelting process. Leaching is performed *in situ*, or in specially prepared piles by distributing acid across the top and allowing it to percolate down through the material where it is collected. The ground under the leach pads is lined with an acid-proof, impermeable plastic material to prevent leach liquor from contaminating groundwater. Once the copper-rich solutions are collected they can be processed by either of two processes—the cementation process or the solvent extraction/electrowinning process (SXEW). In the cementation process (which is rarely used today), the copper in the acidic solution is deposited on the surface of scrap iron in exchange for the iron. When sufficient copper has been cemented out, the copper-rich iron is put into the smelter together with the ore concentrates for copper recovery via the pyrometallurgical route.

In the SXEW process, the pregnant leach solution (PLS) is concentrated by solvent extraction, which extracts copper but not impurity metals (iron and other impurities). The copper-laden organic solution is then separated from the leachate in a settling tank. Sulphuric acid is added to the pregnant organic mixture, which strips the copper into an electrolytic solution. The leachate, containing the iron and other impurities, is returned to the leaching operation where its acid is used

for further leaching. The copper-rich strip solution is passed into an electrolytic cell known as an electrowinning cell. An electrowinning cell differs from an electrorefining cell in that it uses a permanent, insoluble anode. The copper in solution is then plated onto a starting sheet cathode in much the same manner as it is on the cathode in an electrorefining cell. The copper-depleted electrolyte is returned to the solvent extraction process where it is used to strip more copper from the organic solution. The cathodes produced from the electrowinning process are then sold or made into rods in the same manner as those produced from the electrorefining process.

Electrowinning cells are used also for the preparation of starting sheets for both the electrorefining and electrowinning processes by plating the copper onto either stainless steel or titanium cathodes and then stripping off the plated copper.

Hazards and Their Prevention

Prevention of health risks and accidents in the metallurgical industry is primarily an educational and technical question. Medical examinations are secondary and have only a complementary role in the prevention of health risks. A harmonious exchange of information and collaboration between the planning, line, safety and occupational health departments within the company give the most efficient result in the prevention of health risks.

The best and least costly preventive measures are those taken at the planning stage of a new plant or process. In planning of new production facilities, the following aspects should be taken into account as a minimum:

- The potential sources of air contaminants should be enclosed and isolated.
- The design and placement of the process equipment should allow easy access for maintenance purposes.
- Areas in which a sudden and unexpected hazard may occur should be monitored continuously. Adequate warning notices should be included. For example, areas in which arsine or hydrogen cyanide exposure might be possible should be under continuous monitoring.
- Addition and handling of poisonous process chemicals should be planned so that manual handling can be avoided.
- Personal occupational hygiene sampling devices should be used in order to evaluate the real exposure of the individual worker, whenever possible. Regular fixed monitoring of gases, dusts and noise gives an overview of exposure but has only a complementary role in the evaluation of exposure dose.
- In space planning, the requirements of future changes or extensions of the process should be taken into account so that the occupational hygiene standards of the plant will not worsen.

- There should be a continuous system of training and education for safety and health personnel, as well as for foremen and workers. New workers in particular should be thoroughly informed about potential health risks and how to prevent them in their own working environments. In addition, training should be done whenever a new process is introduced.
- Work practices are important. For example, poor personal hygiene by eating and smoking in the worksite may considerably increase personal exposure.
- The management should have a health and safety monitoring system which produces adequate data for technical and economic decision making.

The following are some of the specific hazards and precautions that are found in smelting and refining.

Injuries

The smelting and refining industry has a higher rate of injuries than most other industries. Sources of these injuries include: splattering and spills of molten metal and slag resulting in burns; gas explosions and explosions from contact of molten metal with water; collisions with moving locomotives, wagons, travelling cranes and other mobile equipment; falls of heavy objects; falls from a height (e.g., while accessing a crane cab); and slipping and tripping injuries from obstruction of floors and passageways.

Precautions include: adequate training, appropriate personal protective equipment (PPE) (e.g., hard hats, safety shoes, work gloves and protective clothing); good storage, housekeeping and equipment maintenance; traffic rules for moving equipment (including defined routes and an effective signal and warning system); and a fall protection programme.

Heat

Heat stress illnesses such as heat stroke are a common hazard, primarily due to infrared radiation from furnaces and molten metal. This is especially a problem when strenuous work must be done in hot environments.

Prevention of heat illnesses can involve water screens or air curtains in front of furnaces, spot cooling, enclosed air-conditioned booths, heat-protective clothing and air-cooled suits, allowing sufficient time for acclimatization, work breaks in cool areas and an adequate supply of beverages for frequent drinking.

Chemical hazards

Exposure to a wide variety of hazardous dusts, fumes, gases and other chemicals can occur during smelting and refining operations. Crushing and grinding ore in particular can result in high exposures to silica and toxic metal dusts (e.g., containing lead, arsenic and cadmium). There

can also be dust exposures during furnace maintenance operations. During smelting operations, metal fumes can be a major problem.

Dust and fume emissions can be controlled by enclosure, automation of processes, local and dilution exhaust ventilation, wetting down of materials, reduced handling of materials and other process changes. Where these are not adequate, respiratory protection would be needed.

Many smelting operations involve the production of large amounts of sulphur dioxide from sulphide ores and carbon monoxide from combustion processes. Dilution and local exhaust ventilation (LEV) are essential.

Sulphuric acid is produced as a by-product of smelting operations and is used in electrolytic refining and leaching of metals. Exposure can occur both to the liquid and to sulphuric acid mists. Skin and eye protection and LEV is needed.

The smelting and refining of some metals can have special hazards. Examples include nickel carbonyl in nickel refining, fluorides in aluminium smelting, arsenic in copper and lead smelting and refining, and mercury and cyanide exposures during gold refining. These processes require their own special precautions.

Other hazards

Glare and infrared radiation from furnaces and molten metal can cause eye damage including cataracts. Proper goggles and face shields should be worn. High levels of infrared radiation may also cause skin burns unless protective clothing is worn.

High noise levels from crushing and grinding ore, gas discharge blowers and high-power electric furnaces can cause hearing loss. If the source of the noise cannot be enclosed or isolated, then hearing protectors should be worn. A hearing conservation program including audiometric testing and training should be instituted.

Electrical hazards can occur during electrolytic processes. Precautions include proper electrical maintenance with lockout/tagout procedures; insulated gloves, clothing and tools; and ground fault circuit interrupters where needed.

Manual lifting and handling of materials can cause back and upper extremity injuries. Mechanical lifting aids and proper training in lifting methods can reduce this problem.

Pollution and Environmental Protection

Emissions of irritant and corrosive gases like sulphur dioxide, hydrogen sulphide and hydrogen chloride may contribute to air pollution and cause corrosion of metals and concrete within the plant and in the surrounding environment. The tolerance of vegetation to sulphur dioxide varies depending on the type of forest and soil. In general, evergreen trees tolerate lower concentrations of sulphur dioxide than deciduous ones. Particulate emissions may contain non-specific particulates, fluorides, lead, arsenic, cadmium and many other toxic metals. Wastewater effluent may contain a variety of toxic metals, sulphuric acid and other impurities. Solid wastes can be contaminated with arsenic, lead, iron sulphides, silica and other pollutants.

Smelter management should include evaluation and control of emissions from the plant. This is specialized work which should be carried out only by personnel thoroughly familiar with the chemical properties and toxicities of the materials discharged from the plant processes. The physical state of the material, the temperature at which it leaves the process, other materials in the gas stream and other factors must all be considered when planning measures to control air pollution. It is also desirable to maintain a weather station, to keep meteorological records and to be prepared to reduce output when weather conditions are unfavourable for dispersal of stack effluents. Field trips are necessary to observe the effect of air pollution on residential and farming areas.

Sulphur dioxide, one of the major contaminants, is recovered as sulphuric acid when present in sufficient quantity. Otherwise, to meet emission standards, sulphur dioxide and other hazardous gaseous wastes are controlled by scrubbing. Particulate emissions are commonly controlled by fabric filters and electrostatic precipitators.

Large amounts of water are used in flotation processes such as copper concentration. Most of this water is recycled back into the process. Tailings from the flotation process are pumped as slurry into sedimentation ponds. Water is recycled in the process. Metal-containing process water and rainwater are cleaned in water-treatment plants before discharging or recycling.

Solid-phase wastes include slags from smelting, blowdown slurries from sulphur dioxide conversion to sulphuric acid and sludges from surface impoundments (e.g., sedimentation ponds). Some slags can be reconcentrated and returned to smelters for reprocessing or recovery of other metals present. Many of these solid-phase wastes are hazardous wastes that must be stored according to environmental regulations.

Copper Production Hazards and their prevention

The major hazards are exposure to ore dusts during ore processing and smelting, metal fumes (including copper, lead and arsenic) during smelting, sulphur dioxide and carbon monoxide during most smelting operations, noise from crushing and grinding operations and from furnaces, heat stress from the furnaces and sulphuric acid and electrical hazards during electrolytic processes.

Precautions include: LEV for dusts during transfer operations; local exhaust and dilution ventilation for sulphur dioxide and carbon monoxide; a noise control and hearing protection programme; protective clothing and shields, rest breaks and fluids for heat stress; and LEV, PPE and electrical precautions for electrolytic processes. Respiratory protection is commonly worn to protect against dusts, fumes and sulphur dioxide. Table 1. Process materials inputs and pollution outputs for copper smelting and refining

Process	Material input	Air emissions	Process wastes	Other wastes
Copper concentration	Copper ore, water, chemical reagents, thickeners		Flotation wastewaters	Tailings containing waste minerals such as limestone and quartz
Copper leaching	Copper concentrate, sulphuric acid		Uncontrolled leachate	Heap leach waste
Copper smelting	Copper concentrate, siliceous flux	Sulphur dioxide, particulate matter containing arsenic, antimony, cadmium, lead, mercury and zinc		Acid plant blowdown slurry/sludge, slag containing iron sulphides, silica
Copper conversion	Copper matte, scrap copper, siliceous flux	Sulphur dioxide, particulate matter containing arsenic, antimony, cadmium, lead, mercury and zinc		Acid plant blowdown slurry/sludge, slag containing iron sulphides, silica
Electrolytic copper refining	Blister copper, sulphuric acid			Slimes containing impurities such as gold, silver, antimony, arsenic, bismuth, iron, lead, nickel, selenium, sulphur and zinc

Lead

The primary lead production process consists of four steps: sintering, smelting, drossing and pyrometallurgical refining. To begin, a feedstock comprising mainly of lead concentrate in the form of lead sulphide is fed into a sintering machine. Other raw materials may be added including iron, silica, limestone flux, coke, soda, ash, pyrite, zinc, caustic and particulates gathered from pollution control devices. In the sintering machine the lead feedstock is subjected to blasts of hot air which burn off the sulphur, creating sulphur dioxide. The lead oxide material existing after this process contains about 9% of its weight in carbon. The sinter is then fed along with coke, various recycled and cleanup materials, limestone and other fluxing agents into a blast furnace for reducing, where the carbon acts as a fuel and smelts or melts the lead material. The molten lead flows to the bottom of the furnace where four layers form: “speiss” (the lightest material, basically arsenic and antimony); “matte” (copper sulphide and other metal sulphides); blast furnace slag (primarily silicates); and lead bullion (98% lead, by weight). All layers are then drained off. The speiss and matte are sold to copper smelters for recovery of copper and precious metals. The blast furnace slag which contains zinc, iron, silica and lime is stored in piles and partially recycled. Sulphur oxide emissions are generated in blast furnaces from small quantities of residual lead sulphide and lead sulphates in the sinter feed.

Rough lead bullion from the blast furnace usually requires preliminary treatment in kettles before undergoing refining operations. During drossing, the bullion is agitated in a drossing kettle and cooled to just above its freezing point (370 to 425°C). A dross, which is composed of lead oxide, along with copper, antimony and other elements, floats to the top and solidifies above the molten lead.

The dross is removed and fed into a dross furnace for recovery of the non-lead useful metals. To enhance copper recovery, drossed lead bullion is treated by adding sulphur-bearing materials, zinc, and/or aluminium, lowering the copper content to approximately 0.01%.

During the fourth step, the lead bullion is refined using pyrometallurgical methods to remove any remaining non-lead saleable materials (e.g., gold, silver, bismuth, zinc, and metal oxides such as antimony, arsenic, tin and copper oxide). The lead is refined in a cast iron kettle by five stages. Antimony, tin and arsenic are removed first. Then zinc is added and gold and silver are removed in the zinc slag. Next, the lead is refined by vacuum removal (distillation) of zinc. Refining continues with the addition of calcium and magnesium. These two materials combine with bismuth to form an insoluble compound that is skimmed from the kettle. In the final step caustic soda and/or nitrates may be added to the lead to remove any remaining traces of

metal impurities. The refined lead will have a purity of 99.90 to 99.99% and may be mixed with other metals to form alloys or it may be directly cast into shapes.

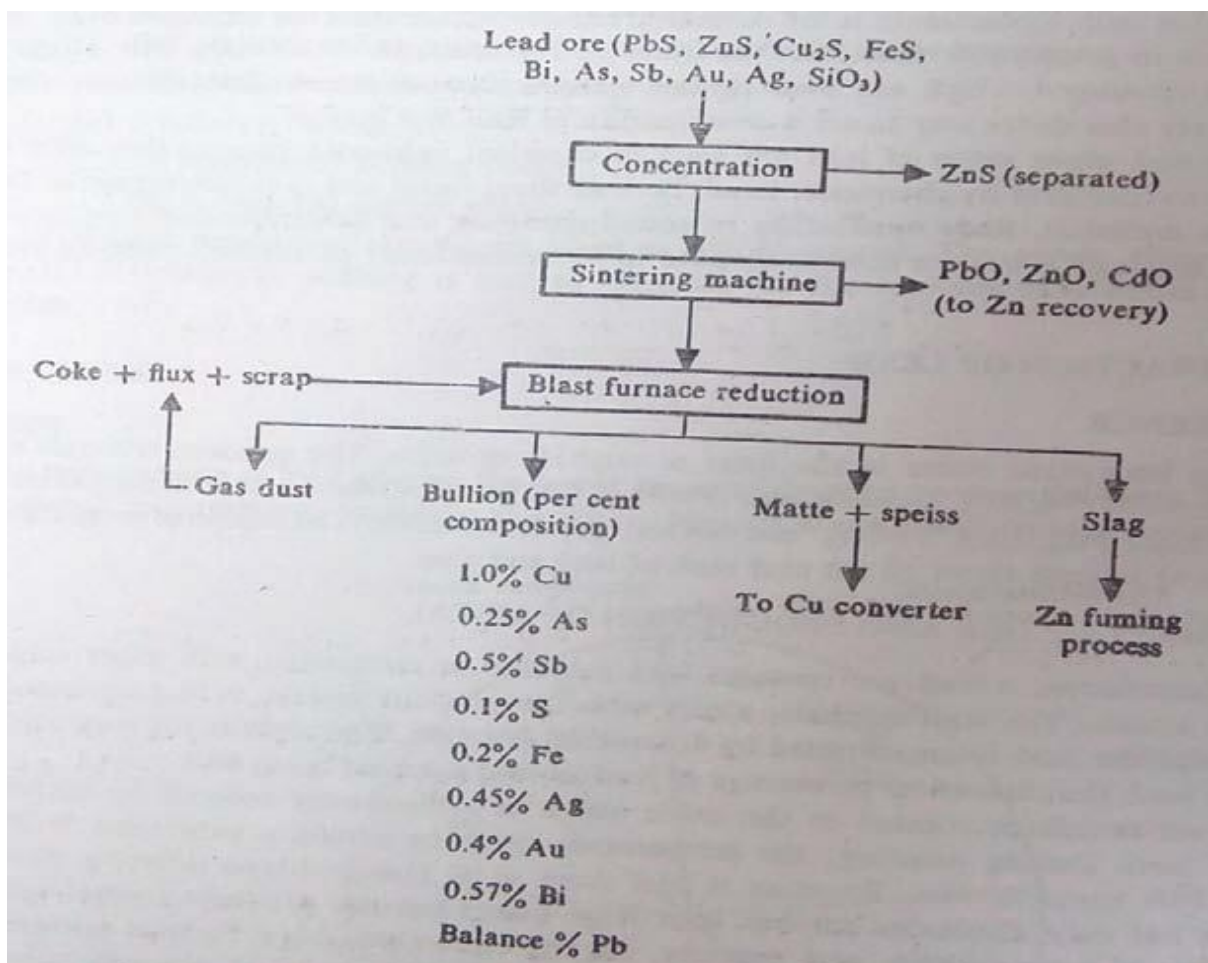


Table 2. Process materials inputs and pollution outputs for lead smelting and refining

Process	Material input	Air emissions	Process wastes	Other wastes
Lead sintering	Lead ore, iron, silica, limestone flux, coke, soda, ash, pyrite, zinc, caustic, baghouse dust	Sulphur dioxide, particulate matter contain-ing cadmium and lead		
Lead smelting	Lead sinter, coke	Sulphur dioxide, particulate matter contain-ing cadmium and lead	Plant washdown wastewater, slag granulation water	Slag containing impurities such as zinc, iron, silica and lime, surface impoundment solids

Lead drossing	Lead bullion, soda ash, sulphur, baghouse dust, coke			Slag containing such impurities as copper, surface impoundment solids
Lead refining	Lead drossing bullion			

Zinc

Zinc concentrate is produced by separating the ore, which may contain as little as 2% zinc, from waste rock by crushing and flotation, a process normally performed at the mining site. The zinc concentrate is then reduced to zinc metal in one of two ways: either pyrometallurgically by distillation (retorting in a furnace) or hydrometallurgically by electrowinning. The latter accounts for approximately 80% of total zinc refining.

Four processing stages are generally used in hydrometallurgic zinc refining: calcining, leaching, purification and electrowinning. Calcining, or roasting, is a high-temperature process (700 to 1000 °C) that converts zinc sulphide concentrate to an impure zinc oxide called calcine. Roaster types include multiple-hearth, suspension or fluidized-bed. In general, calcining begins with the mixing of zinc-containing materials with coal. This mixture is then heated, or roasted, to vaporize the zinc oxide which is then moved out of the reaction chamber with the resulting gas stream. The gas stream is directed to the baghouse (filter) area where the zinc oxide is captured in baghouse dust.

All of the calcining processes generate sulphur dioxide, which is controlled and converted to sulphuric acid as a marketable process by-product.

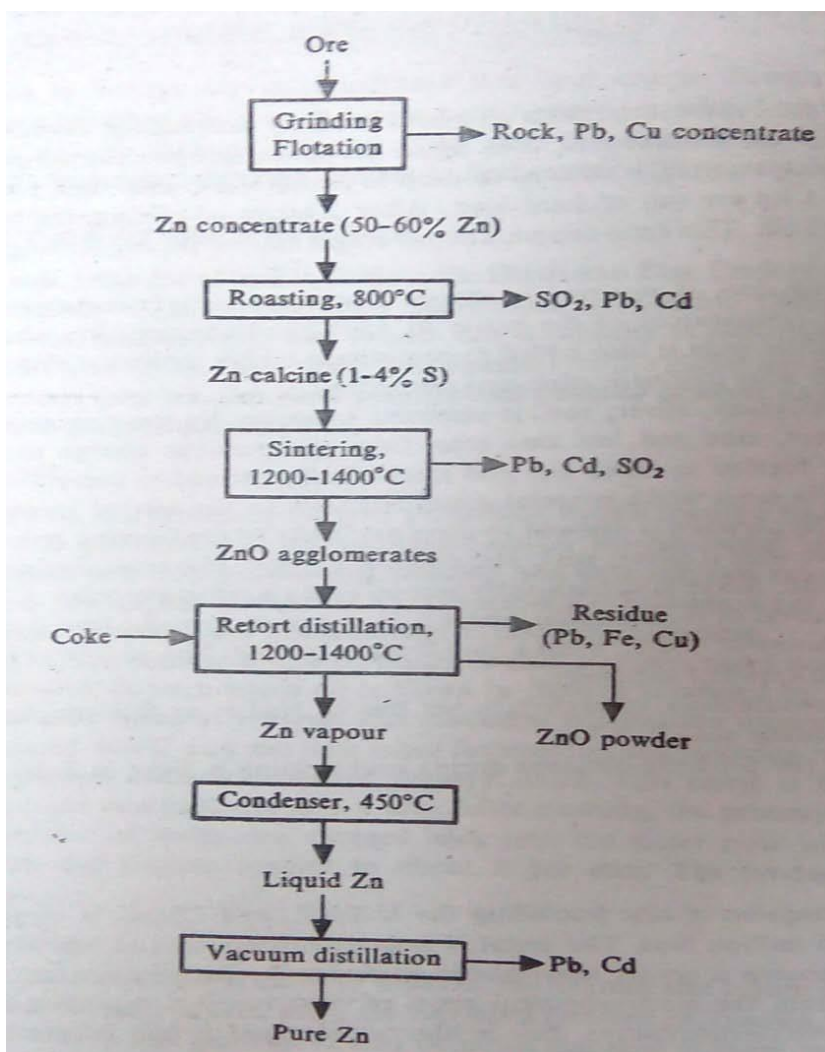
Electrolytic processing of desulphurized calcine consists of three basic steps: leaching, purification and electrolysis. Leaching refers to the dissolving of the captured calcine in a solution of sulphuric acid to form a zinc sulphate solution. The calcine may be leached once or twice. In the double-leach method, the calcine is dissolved in a slightly acidic solution to remove the sulphates. The calcine is then leached a second time in a stronger solution which dissolves the zinc. This second leaching step is actually the beginning of the third step of purification because many of the iron impurities drop out of the solution as well as the zinc.

After leaching, the solution is purified in two or more stages by adding zinc dust. The solution is purified as the dust forces deleterious elements to precipitate so that they can be filtered out. Purification is usually conducted in large agitation tanks. The process takes place at temperatures ranging from 40 to 85°C and pressures ranging from atmospheric to 2.4 atmospheres. The elements recovered during purification include copper as a cake and cadmium as a metal. After purification the solution is ready for the final step, electrowinning.

Zinc electrowinning takes place in an electrolytic cell and involves running an electric current from a lead-silver alloy anode through the aqueous zinc solution. This process charges the suspended zinc and forces it to deposit onto an aluminium cathode which is immersed in the solution. Every 24 to 48 hours, each cell is shut down, the zinc-coated cathodes removed and rinsed, and the zinc

mechanically stripped from the aluminium plates. The zinc concentrate is then melted and cast into ingots and is often as high as 99.995% pure.

Electrolytic zinc smelters contain as many as several hundred cells. A portion of the electrical energy is converted into heat, which increases the temperature of the electrolyte. Electrolytic cells operate at temperature ranges from 30 to 35°C at atmospheric pressure. During electrowinning a portion of the electrolyte passes through cooling towers to decrease its temperature and to evaporate the water it collects during the process.



Hazards and their prevention

The major hazards are exposure to ore dusts during ore processing and smelting, metal fumes (including zinc and lead) during refining and roasting, sulphur dioxide and carbon monoxide during most smelting operations, noise from crushing and grinding operations and from furnaces, heat stress from the furnaces and sulphuric acid and electrical hazards during electrolytic processes.

Precautions include: LEV for dusts during transfer operations; local exhaust and dilution ventilation for sulphur dioxide and carbon monoxide; a noise control and hearing protection programme; protective clothing and shields, rest breaks and fluids for heat stress; and LEV, PPE, and electrical precautions for electrolytic processes. Respiratory protection is commonly worn to protect against dusts, fumes and sulphur dioxide.

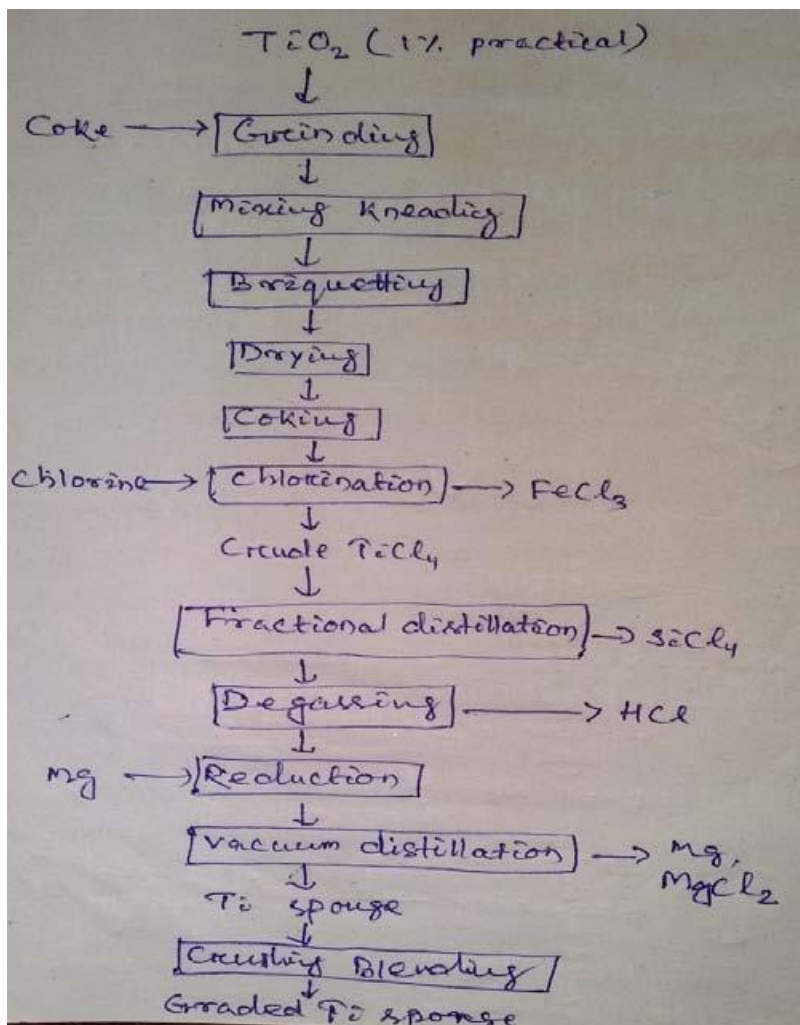
Table 3. Process materials inputs and pollution outputs for zinc smelting and refining

Process	Material input	Air emissions	Process wastes	Other wastes
Zinc calcining	Zinc ore, coke	Sulphur dioxide, particulate matter containing zinc and lead		Acid plant blowdown slurry
Zinc leaching	Zinc calcine, sulphuric acid, limestone, spent electrolyte		Wastewaters containing sulphuric acid	
Zinc purification	Zinc-acid solution, zinc dust		Wastewaters containing sulphuric acid, iron	Copper cake, cadmium
Zinc electrowinning	Zinc in a sulphuric acid/aqueous solution, lead-silver alloy anodes, aluminium cathodes, barium carbonate or strontium, colloidal additives		Dilute sulphuric acid	Electrolytic cell slimes/sludges

Titanium

Synthetic rutile is a chemically modified form of ilmenite which has had most of the iron removed. The product's composition is between 85 and 95 per cent titanium dioxide (TiO₂). The upgraded TiO₂ products are similar to naturally formed rutile. Ilmenite, an iron/titanium oxide mineral, can be upgraded to synthetic rutile (or upgraded ilmenite) containing between 85 and 95 per cent highly valued titanium dioxide. Iluka has four synthetic rutile kilns with a combined capacity of 500 – 550 thousand tonnes per annum. The ilmenite used in the process generally has between 57 and 60 per cent TiO₂ and yields about 0.6 tonnes of SR for every tonne of ilmenite used. The main

objective of the process is to remove the iron component of the ilmenite by reducing it to metal and “leaching” it to leave an upgraded titania product. This process is known as the Becher Process, after its inventor, Dr Robert Becher, who developed the process in Western Australia in 1961. The process was commercialised by Iluka’s predecessor company, RGC, in 1969



Titanium (Ti) is a soft, ductile, silvery gray metal with a melting point of $1,675\text{ }^{\circ}\text{C}$ ($3,047\text{ }^{\circ}\text{F}$). Owing to the formation on its surface of an oxide film that is relatively inert chemically, it has excellent corrosion resistance in most natural environments. In addition, it is light in weight, with a density (4.51 grams per cubic centimetre) midway between aluminum and iron. Its combination of low density and high strength gives it the most efficient strength-to-weight ratio of common metals for temperatures up to $600\text{ }^{\circ}\text{C}$ ($1,100\text{ }^{\circ}\text{F}$).

Because its atomic diameter is similar to many common metals such as aluminum, iron, tin, and vanadium, titanium can easily be alloyed to improve its properties. Like iron, the metal can exist in two crystalline forms: hexagonal close-packed (hcp) below $883\text{ }^{\circ}\text{C}$ ($1,621\text{ }^{\circ}\text{F}$) and body-centred cubic (bcc) at higher temperatures up to its melting point. This allotropic behaviour and the capacity to alloy with many elements result in titanium alloys that have a wide range of mechanical and corrosion-resistant properties. Although titanium ores are abundant, the high reactivity of the

metal with oxygen, nitrogen, and hydrogen in the air at elevated temperatures necessitates complicated and therefore costly production and fabrication processes. Titanium ore was first discovered in 1791 in Cornish beach sands by an English clergyman, William Gregor. The actual identification of the oxide was made a few years later by a German chemist, M.H. Klaproth. Klaproth gave the metal constituent of this oxide the name titanium, after the Titans, the giants of Greek mythology.

Pure metallic titanium was first produced in either 1906 or 1910 by M.A. Hunter at Rensselaer Polytechnic Institute (Troy, New York, U.S.) in cooperation with the General Electric Company. These researchers believed titanium had a melting point of 6,000 °C (10,800 °F) and was therefore a candidate for incandescent-lamp filaments, but, when Hunter produced a metal with a melting point closer to 1,800 °C (3,300 °F), the effort was abandoned. Nevertheless, Hunter did indicate that the metal had some ductility, and his method of producing it by reacting titanium tetrachloride (TiCl₄) with sodium under vacuum was later commercialized and is now known as the Hunter process. Metal of significant ductility was produced in 1925 by the Dutch scientists A.E. van Arkel and J.H. de Boer, who dissociated titanium tetraiodide on a hot filament in an evacuated glass bulb.

In 1932 William J. Kroll of Luxembourg produced significant quantities of ductile titanium by combining TiCl₄ with calcium. By 1938 Kroll had produced 20 kilograms (50 pounds) of titanium and was convinced that it possessed excellent corrosion and strength properties. At the start of World War II he fled Europe and continued his work in the United States at the Union Carbide Company and later at the U.S. Bureau of Mines. By this time, he had changed the reducing agent from calcium to magnesium metal. Kroll is now recognized as the father of the modern titanium industry, and the Kroll process is the basis for most current titanium production. A U.S. Air Force study conducted in 1946 concluded that titanium-based alloys were engineering materials of potentially great importance, since the emerging need for higher strength-to-weight ratios in jet aircraft structures and engines could not be satisfied efficiently by either steel or aluminum. As a result, the Department of Defense provided production incentives to start the titanium industry in 1950. Similar industrial capacity was founded in Japan, the U.S.S.R., and the United Kingdom. After this impetus was provided by the aerospace industry, the ready availability of the metal gave rise to opportunities for new applications in other markets, such as chemical processing, medicine, power generation, and waste treatment.

Ores

Titanium is the fourth most abundant structural metal on Earth, exceeded only by aluminum, iron, and magnesium. Workable mineral deposits are dispersed worldwide and include sites in Australia, the United States, Canada, South Africa, Sierra Leone, Ukraine, Russia, Norway, Malaysia, and several other countries.



Rutile; pyrophyllite Rutile on pyrophyllite from Mono County, California. *B.M. Shaub*

The predominate minerals are rutile, which is about 95 percent [titanium dioxide](#) (TiO_2), and ilmenite (FeTiO_3), which contains 50 to 65 percent TiO_2 . A third mineral, leucoxene, is an alteration of ilmenite from which a portion of the iron has been naturally leached. It has no specific titanium content. Titanium minerals occur in alluvial and volcanic formations. Deposits usually contain between 3 and 12 percent heavy minerals, consisting of ilmenite, rutile, leucoxene, zircon, and monazite.

Mining And Concentrating

Although workable known reserves of rutile are diminishing, ilmenite deposits are abundant. Typical mining is by open pit. A suction bucket wheel on a floating dredge supplies a mineral-rich sand to a set of screens called trommels, which remove unwanted materials. Typically, the minerals are separated from waste material by gravity separation in a wet spiral concentrator. The resulting concentrates are separated by passing them through a complex series of electrostatic, magnetic, and gravity equipment.

Extraction and Refining - TiCl_4

The production of titanium metal accounts for only 5 percent of annual titanium mineral consumption; the rest goes to the titanium pigment industry. Pigments are produced using either a [sulfate process](#) or a more environmentally acceptable carbo-chlorination process (described below) that converts TiO_2 into TiCl_4 . The latter process also supplies the TiCl_4 necessary for the production of titanium metal.

Environmental and economic constraints dictate that the ore feed stocks converted by carbo-chlorination processes now in use contain greater than 90 percent TiO_2 . Only natural rutile meets this requirement, but ilmenite can be upgraded through combinations of pyrometallurgical and hydrometallurgical techniques to produce a [synthetic](#) rutile of 90 to 93 percent TiO_2 . In addition, titaniferous magnetite ores can be smelted to produce [pig iron](#) and titanium-rich slags. Rutile,

leucoxene, synthetic rutile, and slag can then be mixed to provide a feed stock of more than 90 percent TiO₂ for the chlorination process.

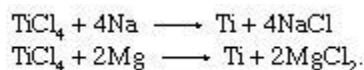
In the first step of this process, the oxide ores are reacted with chlorine in a fluidized bed of petroleum coke. Oxygen combines with carbon (C) in the coke to produce [carbon monoxide](#) (CO) and [carbon dioxide](#) (CO₂), while the titanium and chlorine react to form a gaseous TiCl₄, as in the following reaction:



(The X and Y represent variable quantities whose ratio depends on the reaction temperature, which varies between 850 and 1,000 °C [1,550 and 1,800 °F].) The raw TiCl₄ is cleaned of fine particles of entrained coke and titanium ore, and then it is liquified and passed through a distillation column to remove volatile impurities of both high and low boiling points. Vanadium oxychloride, an impurity with a [boiling point](#) similar to TiCl₄, is stripped from the product stream by reaction with [mineral oil](#). The TiCl₄ is then redistilled to remove other impurities in a reflux distillation column. This process produces TiCl₄ of a purity exceeding 99.9 percent. Since any contaminants in the TiCl₄ would later be reduced along with the titanium metal, high-quality TiCl₄ must be produced to achieve high-quality metal.

Titanium sponge

In the production of titanium [pigments](#), the TiCl₄ would be reoxidized to TiO₂, but, in the production of titanium metal, it is reduced with either sodium (Na) in the Hunter process or with magnesium (Mg) in the [Kroll process](#):



These reactions take place in large, sealed steel vessels at approximately 800 to 1,000 °C (1,450 to 1,800 °F) in an inert argon atmosphere to avoid contamination of the final product by air or moisture. Both processes produce titanium in the form of a highly porous material called sponge, with the salts NaCl or MgCl₂ entrapped in the pores. The sponge is crushed, and the metal and salts are separated by either a dilute acid leach or by high-temperature vacuum distillation. The salts are recycled through electrolytic cells to produce sodium or magnesium for reuse in metal reduction and chlorine for reuse in chlorination of the ore. A different process that offers hope for an improved and simplified method of producing titanium metal is the direct electrowinning of titanium from TiCl₄ in fused chloride salt baths. In this case, titanium sponge collects on a steel cathode, and chlorine gas is given off at the carbon anode. The required use in this process of high-melting-point salts, combined with the need for maintaining an inert [environment](#), present major technical and economical hurdles that have to be overcome in order to achieve commercial status.

Titanium Ingot

The conversion of purified titanium sponge to a form useful for structural purposes involves several steps. Consolidation into titanium ingot is performed in a vacuum or argon environment by the consumable-electrode arc-melting process. [Sponge](#), alloying elements, and in some cases recycled scrap are first mechanically compacted and then welded into a long, cylindrical electrode.

The electrode is melted vertically into a water-cooled copper crucible by passing an electric current through it. To ensure uniform distribution of alloying elements, this primary ingot is remelted at least once in a similar manner. Ingots weigh between 4 and 10 tons and are up to 1,050 millimetres (42 inches) in diameter.

Cold-hearth melting is an alternate consolidation process that is conducted inside an argon or vacuum chamber containing a water-cooled, horizontal copper crucible. Heating is accomplished by multiple electron-beam or by argon/helium plasma torches. The molten metal flows in a horizontal path over the lip of the hearth into a suitably shaped, water-cooled copper mold. The cold-hearth process is well suited to separating high-density contaminants, which settle to the bottom of the hearth. For this reason, it is used primarily to recycle titanium scrap, which can contain carbide tool bits left over from machining operations. Consolidated ingots are processed into mill products such as bar, billet, wire, tubing, plate, and sheet by traditional steel facilities.

Using the common phases present at room temperature, titanium alloys are divided into four classes: commercially pure, alpha, alpha-beta, and beta. Each class has distinctive characteristics. Pure titanium, although very ductile, has low strength and is therefore used when strength is not critical and corrosion resistance is desired. The alpha alloys are weldable and have good elevated-temperature strengths. The alpha-beta alloys are widely used because of their good combinations of strength, toughness, and formability. The beta alloys are useful where very high tensile strengths are required.

There are three important markets for titanium metal: aerospace, nonaerospace industries, and alloy additives. The aerospace and industrial markets utilize mill products, while the alloy-additive market consumes lower-cost titanium units such as scrap and sponge. Small additions of titanium (less than 1 percent) are added to other metals such as nickel, aluminum, and iron in order to improve formability and mechanical properties.

Aerospace applications

The aerospace market is still the most important, with titanium products being used in both commercial and military aircraft. Gas turbines account for nearly half of annual titanium production. Titanium alloys are utilized principally in the fan and compressor sections at temperatures up to 600 °C. Typical parts include inlet cases, compressor blades, disks, and hubs, as well as spacers and seals. The large high-bypass turbofan engines utilized on wide-body commercial airliners could not have been developed without strong, lightweight titanium alloys. These engines are greater than 25 percent by weight titanium.

Titanium alloys are also utilized in airframes because of their high strength-to-weight ratios, good toughness, and corrosion resistance. The titanium content of airframes can range from as low as 2 percent to as high as 30 percent by weight. Typical commercial airframes are 4 to 8 percent titanium, while many military aircraft contain greater amounts. The metal is used in fasteners, landing-gear supports, springs, fail-safe straps, and numerous internal bulkhead and wing-support components.

Non aerospace applications

The resistance of titanium to many corrosive environments, particularly oxidizing and chloride-containing process streams, has led to widespread industrial applications. Titanium is resistant to all natural environments, including natural waste products, body fluids, and salt and brackish water; to most salt solutions, including chlorides, bromides, iodides, and sulfides; and to most oxidizing acids, organic acids, and alkaline solutions.

When strength is not a major consideration, commercially pure titanium is the material of choice because of its lower cost, ease of fabrication, and good corrosion resistance. Alloys such as Ti–0.15Pd, Ti–0.3Mo–0.8Ni, and Ti–3Al–8V–6Cr–4Mo–4Zr can extend the usefulness of the metal to either higher temperatures or stronger concentrations of reducing acids and acidic salts. In recent years, more high-strength alloys have been utilized for corrosion applications. For example, Ti–6Al–4V, a versatile alloy that was developed in the 1950s for the aerospace industry, has become a very important material for medical prostheses such as hip-joint replacements because of its strength-to-weight ratio and immunity to body fluids. Ti–3Al–8V–6Cr–4Mo–4Zr, an even stronger alloy, also has excellent resistance to high-temperature sour gas (natural gas containing hydrogen sulfide) and is therefore used in energy extraction for downhole tubing and casings and for instrumentation.

Several industrial processes have been improved as a result of the availability of titanium. After titanium was introduced as a replacement for stainless-steel diffusion washers in the pulp and paper industry, the metal's excellent performance encouraged the design of new displacement bleaching systems using up to 35 tons of titanium components. Typical parts include diffusers, central shafts, scrapers, filtrate pumps, heat exchangers, packing boxes, and valves. In the early 1960s it was discovered that coating titanium with a platinum-group metal or metal oxide produced an anode (a negatively charged electrode) that was slow to corrode in electrolytic solutions. Coated titanium anodes soon replaced graphite anodes in the chlorine industry, resulting in lower costs and products of higher purity. Extensions of this technology are now being applied to electrogalvanizing and tin-coating processes.

Chemical-process industries utilize titanium heat exchangers to eliminate corrosion problems caused by cooling waters containing chloride and sulfide, and several benefits can accrue from employing titanium on the process side of heat exchangers as well. Because the metal is resistant to erosion corrosion, titanium vessels can be subjected to process liquids flowing at high rates, thereby eliminating the danger of biofouling. In addition, titanium is the only metal known to be completely resistant to all forms of biofouling corrosion. These advantages, along with its light weight, make the metal desirable for heat exchangers in naval vessels and offshore oil platforms.

Titanium is gaining greater recognition in consumer applications, such as eyeglass frames, watches, sports equipment, jewelry, high-performance automobiles, and roofing. Other possible applications include valves for automobile engines, scrubbers for flue-gas desulfurization, marine and offshore risers, joints and fittings, and nuclear-waste storage and transportation casks.

Ferro Nickel Production

Ferronickel is vital importance to modern society. It is because ferronickel is main feedstock in stainless steel production. Without stainless steel, we would not be able to enjoy many of the things that we take for granted, such as stainless-steel appliances in our home and workplaces and computer.

There are two types of nickel ore on earth: nickel sulfide and nickel oxide. Nickel oxide ore is usually called laterite, which represents 61% nickel ore on earth and 40% of world is in the form of laterite. Laterite ore normally classified into two groups:

Limonite, which occur near the surface and easily mined. Limonite layer consists of a mixture of minerals that have a high iron and low MgO content. The general formula of goethite, $(\text{Fe,Ni})\text{OOH}$, is used to represent limonite ores in chemical reactions. Saprolite, occur below limonite on the earth crust and the saprolite ores have a low iron and a high MgO content. Because it is further from the surface, it is less weathered or chemically altered, than limonite. The minerals found in this layer are magnesium and hydroxysilicates with generic formula of $(\text{Mg}[\text{Ni,Co}]_3\text{Si}_2\text{O}_5(\text{OH})_4)$, is used to represent saprolite ores in chemical reactions.

Feed material for ferronickel production is predominantly Saprolite, rather than Limonite. This is because the iron content of the saprolite ore about 15% Fe, is lower than that of limonite ore. The choice of saprolite ore ensures that the ferronickel product is not excessively diluted by iron. Production process of ferronickel consists of four main steps.

Drying: elimination of most or a substantial portion of free moisture content of the nickel ore

Calcination-reduction: elimination of the remainder of the free ore moisture and its crystalline water, preheating of the ore, and reduction of a substantial portion of the nickel and a controlled portion of the iron

Electric furnace smelting: completion of reduction of the nickel separation of the product ferronickel

Refining: elimination of undesirable minor elements from the ferronickel to meet market specification

Production of ferro-nickel by pyrometallurgical process is still the most widely utilized method for the processing of nickel lateritic ores. The Ni-content of lateritic ore is normally low and in the range of 0.8 - 3 %. The most important production route is the RKEF (rotary kiln - electric furnace) process. For this route lateritic ore is screened, crushed and blended to produce a consistent process plant feed with defined ratios of iron and nickel as well as SiO_2 and MgO. This feed is charged into a rotary kiln where it is calcined and pre-reduced by coal or powdered coke. Afterwards the calcine and residual coke is charged into the electric furnace (also named submerged arc furnace (SAF)). Here it is melted by electric energy and reduced yielding crude FeNi with Ni contents usually between 13 and 25 %. Unreduced components (mainly FeO, SiO_2 , MgO) are removed as slag whereas crude FeNi metal is tapped semi-continuously into ladles.

This crude metal contains undesirable tramp elements such as sulfur, phosphorous, carbon and silicon. Especially sulfur and phosphorous are very unwanted in the steel production where most

of the FeNi is used as alloying element. Therefore, the tramp elements must be removed before the FeNi is cast into bars or granulated. Low carbon contents are necessary to minimize the carbon input during steel production, which would lead to longer treatment times in the stainless-steel refining process. Due to differences in the lateritic deposits regarding nickel oxide and iron oxide content, the content of impurities, sulfur content in the reductant coke etc. the chemical composition of the crude FeNi varies widely (e.g. carbon content can be up to 2 %, sulfur content up to 1 %).