The Complete Book on Non-Ferrous and Precious Metals with Electroplating Chemicals
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Non-ferrous metals are those which don’t have any iron content. These are specified for structural applications requiring reduced weight, higher strength, nonmagnetic properties, higher melting points, or resistance to chemical, atmospheric corrosion and also for electrical and electronic applications.

A precious metal is a rare, naturally occurring metallic chemical element of high economic value. Although they have industrial uses, they are better known for their uses in art, jewellery and coinage. Depending on the end use, metals can be simply cast into the finished part, or cast into an intermediate form, such as an ingot, then worked, or wrought, by rolling, forging, extruding, or other deformation process.

Electroplating is a procedure that uses electrolysis to apply a thin layer of a metal over the surface of another metal. Electroplating chemicals are used to change the surface properties of an object such as abrasion and wear resistance, corrosion protection, lubricity, etc. This chemical is widely demanded in automotive, electronics, telecommunications, aerospace and precision engineering industries. This handbook explains different extraction and production processes with flow diagrams of various non-ferrous and precious metals.

Major contents of the book are Silver, Gold, Copper, Complex salts of copper, silver and gold, magnesium, chromium, platinum group of metals, nickel, zinc, lead, aluminium, mercury, cobalt, sodium, sodium chloride, soda ash, sodium sulfate, glauber salt, hydrochloric acid, sodium silicate, sodium sulfides, sodium thiosulfate, sodium bisulfate, anhydrous, sodium hyposulfite, liquid chlorine, hydrides of boron, silicon, sulfuric acid, nitric acid, ammonium nitrate, hydrazine, hydrogen cyanide, melamine, amines, aniline, isocyanates, phosphorus, tin, ferroalloys, manganese, bismuth, cerium, phosphoric acid, tungsten, niobium and tantalum etc.

It will be a standard reference book for professionals, entrepreneurs, engineers, those studying and researching in this important area and others interested in the field of non-ferrous, precious metals and electroplating chemicals.

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Silver
The common ores of silver are argentite (Ag₂S) and cerargyrite (AgCl). Virtually all naturally occurring gold deposits contain some silver; the amount usually being sufficient to meet the cost of refining the impure gold bullion. Argentite is closely associated with ores of lead, copper, and zinc. Hence, silver is largely produced as a byproduct. It has been computed that about 75 per cent of the total world output of silver is derived from the refining of base metals and only about 25 per cent from silver ore proper.

Extraction by Chloridizing Roasting
Sulphide ores of silver can be successfully subjected to chloridizing roasting with common salt. A solid-state roasting usually produces impure AgCl contaminated with base metals, and attempts to leach out AgCl using hot brine have not been very successful. More efficient leaching is achieved by using a hot solution of hyposulphite, silver being subsequently recovered as a sulphide by precipitation with sodium sulphide. During the precipitation step, the hyposulphite is regenerated and can be recirculated. The precipitation reaction is

\[ 2\text{AgNa}_2\text{S}_2\text{O}_3 + \text{Na}_2\text{S} = 2\text{Na}_2\text{S}_2\text{O}_3 + \text{Ag}_2\text{S}. \]

Silver can be recovered from Ag₂S by dissolution in acid. Alternatively, the sulphide can be roasted and reduction smelted along with lead to give a lead bullion. The process for the recovery of silver from the lead bullion.

Extraction by Cyanidation
Silver can be recovered from its ores by cyanidation. The process is similar to that employed for gold. It should, however, be noted that in the case of silver, as compared with gold, cyanidation requires more cyanide on a weight basis because silver has a lower atomic weight. Also, cementation consumes more zinc and the time required for the dissolution of the ore is greater.

Gold
Extraction of Gold
Gold is widely distributed in nature in both the native and combined forms. The native metal occurs in the form of grains or particles that are disseminated through veins of quartz and other rocks or are intermixed with river-bed sands. The metal is invariably alloyed with silver. Small quantities of gold are often associated with ores of lead, copper, and zinc.

Gold is generally extracted by any one of the following processes:

1. The amalgamation process.
2. The cyanidation process.
3. The chlorination process.

Each of these processes is preceded by a preliminary concentration step. The metal may be liberated from the quartzite rock matrix itself by crushing and grinding. Recently, some advances have been made with regard to the separation of a substantial fraction of silica from the quartz rock by flotation. Oxides of metals such as iron and antimony, which are sometimes present in the quartz rock, can also be removed by this process. Gravity concentration methods also seem promising because gold is a very heavy metal.

Amalgamation Process
The amalgamation process, developed centuries ago, is now almost obsolete. In this process, a slurry made up of the wet ground gold ore is allowed to flow down a sloping surface lined with copper. The surface is continuously washed with an amalgam of silver and mercury. The amalgam takes up gold from the slurry, and the metal is subsequently recovered from the amalgam by distilling off mercury. The amalgamation process yields a low recovery of gold, i.e., only 40–60 per cent. The substantial gold loss can be attributed to several factors. First, very fine fractions of the rock particles have a tendency to float up.
thus allowing the accompanying gold to escape amalgamation. Second, metal particles which are completely embedded in the rock fractions do not get amalgamated. Finally, crushing and grinding may introduce some grease and oil which would also interfere with the absorption of gold by the amalgam. It should be noted that the amalgamation process is very sensitive to the nature of the ore. For example, an ore containing a sulphide would lead to a particularly low recovery because the gold particles remain surrounded by the sulphide even after considerable amount of grinding has been carried out.

Chlorination Process
The chlorination process aims at chlorinating an ore of gold at high temperatures to produce soluble gold chloride (AuCl3). Gold may be subsequently precipitated as a sulphide by passing H2S through the solution. Finally, the sulphide is smelted to yield the metal. Although the process seems simple, it had never been popular in the past mainly due to the problems faced while handling chlorine. With the development of better corrosion-resistant materials in recent years, chlorination reactions, in general, are finding increasing application, and the feasibility of this particular approach may be reassessed.

Chromium
Uses
Metallic chromium is chiefly used for alloying purposes. The nickel alloys that contain chromium form a special class; i.e., they exhibit a remarkable resistance to both high-temperature oxidation and corrosion. In the case of most other alloys, i.e., those in which chromium is present along with iron, ferrochromium, which is easier to produce than metallic chromium, is employed as an alloying agent. In austenitic and ferritic stainless steels, which are widely used in chemical processing, oil refining, and food processing, ferrochromium is used as the alloying element.

Occurrence
Chromium occurs in nature as chromite (FeO·Cr2O3). Since either Fe2O3 or Al2O3 can replace Cr2O3 in the chromite grains, the grade of the chromite varies over a wide range. The ore is upgraded by sorting and hand-picking and beneficiated by flotation so as to reject undesirable magnesium silicates and also by magnetic separation. In practice, upgrading is not necessary because high-grade deposits are available to meet the present requirements. The main chromite deposits are found in South Africa, Zimbabwe, Turkey, and the U.S.S.R. India also has sizeable deposits of chromite ores.

Electrolytic Chromium
Chrome Alum Process
In the chrome alum process, ferrochromium with a high carbon content is converted to NH4Cr(SO4)2·12H2O by first dissolving it in H2SO4 and then adding (NH4)2SO4. Ammonium chromium sulphate is electrolyzed in a cell with a diaphragm. This diaphragm is used to prevent the sulphuric acid and the chromic acid formed at the anode from mixing with the catholyte and oxidizing the divalent chromium. The breakdown of the composition of the electrolyte in the various compartments of the cell is given in Table 1. The cell is operated at 4.2 V at 53°C at a current density of 8 A/mm2 with a current efficiency of 45 per cent.

Nickel
Smelting of Nickel Concentrate
As in the case of copper; nickel, too, has to be separated from the iron present in the sulphide concentrate. In the conventional process, this is done in both the smelting and converting stages. To aid iron rejection in the smelting stage, the concentrate is first partially roasted to selectively oxidize the iron sulphide. This is done either in a multiple hearth roaster or in a fluid bed roaster. The latter is preferred because of its high throughput and the rich SO2 gas stream it generates. During partial roasting in the temperature range 550-600°C, about 40 per cent of the sulphur is oxidized and enough heat is generated to make the roasting in the fluid bed autogenous.
The roasted calcine, which also contains the desired amount of siliceous flux, is smelted in a reverberatory furnace to produce a matte containing the Cu and Ni values and a slag containing the gangue and oxidized iron. The matte typically contains 20 per cent Ni, 7 per cent Cu, 40 per cent Fe, and 27 per cent S. The converter slags from both the nickel and copper converters are returned to the reverberatory furnace. Hence, there is a copper pick-up in the circuit. The discard slag from the reverberatory furnace typically analyzes 0.3-0.4 per cent Ni, 0.2 per cent Cu, 39 per cent Fe, and 35 per cent SiO2.

The furnace matte is converted in a Pierce-Smith converter to produce nickel-enriched matte with 50 per cent Ni, 25 per cent Cu, 0.7 per cent Fe, and 21.5 per cent S. The converting is completed at about 1150ºC to produce matte with the aforesaid desired sulphur content. The slag, containing about 2 per cent Ni, 1.5 per cent Cu, 40 per cent Fe, and 25 per cent SiO2, is returned to the reverberatory furnace for the recovery of nickel and copper.

The converter matte is subjected to a slow cooling process wherein the matte is cooled from its melting point to about 400ºC in a period of 3 days. During slow cooling, first Cu2S precipitates and grows. At 700ºC, a second phase, namely, a metallic nickel-copper alloy phase, starts to precipitate. At 575ºC the third solid phase, Ni3S2, starts to precipitate. The slow cooling rate provides the necessary grain growth so that in subsequent processing the sulphides can be recovered by froth flotation.

The slow-cooled matte is subjected to grinding and flotation. Here diphenyl guanidine (DPG) is used both as a collector and a frother rather than xanthate because the former has been found to be more effective. Prior to flotation, the nickel-copper alloy, which contains over 95 per cent of the precious metals, is isolated by magnetic separation and sent for the recovery of precious metals. The copper sulphide concentrate produced by flotation contains about 70 per cent Cu, 5 per cent Ni, and 20 per cent S and is sent to the copper circuit. The nickel sulphide is recovered as a low copper-nickel sulphide with 74 per cent Ni, 0.8 per cent Cu, 0.8 per cent Fe, and 22 per cent S and as a high copper-nickel sulphide with 72 per cent Ni, 3-4 per cent Cu, 0.8 per cent Fe, and 21 per cent S. Both the nickel sulphide fractions are roasted after pelletization in fluid bed roasters in the temperature range 1100-1250ºC to produce granular nickel oxide.

Carbonyl Process for Refining Nickel
In 1889, Carl Langer and Ludwig Mond discovered a novel process for refining nickel. They found that carbon monoxide combined with metallic nickel in the temperature range 40-90ºC to form gaseous nickel carbon [Ni(CO)4]. At higher temperatures, i.e., between 150 and 300ºC, the nickel carbonyl decomposes to give pure nickel and carbon monoxide.

Zinc
Uses
The annual global consumption of zinc (excluding the U.S.S.R. and China) is comparable with that of lead, i.e., about 5 million tons. The metal is most extensively used as a protective coating for steel (galvanizing) because it resists atmospheric corrosion by forming an impervious basic zinc carbonate layer. From the electrochemical point of view, too, a zinc coating protects steel because the former is more electropositive. Zinc is also widely used in the fabrication of alloys such as Cu-Zn brasses. A low melting point, a relatively high structural strength, a good dimensional stability, and a relatively low cost per unit weight render zinc ideal for die casting. Rolled zinc plates are used in dry cell batteries. The formability of the metal makes it suitable for forging and extrusion. Finally, zinc is used in combination with other compounds in the manufacture of paints and pigments.

In India, galvanizing consumes the maximum amount of zinc (about 60 per cent). This is followed by the metal's use in the manufacture of brass and zinc oxide. Die casting accounts for only about 10 per cent of
the metal.

Vertical Retort Reduction

Vertical retorts are usually made of silicon carbide because it has a conductivity that is about five times higher than that of clay. Consequently, in comparison with a horizontal retort, a vertical retort has much thicker walls, is much larger in size (height approximately 10 m, diameter 0.7 m, and thickness 30 cm), and has a much higher capacity (7-10 tons of zinc per day). Most retorts are provided with automatic charging and discharging mechanisms which facilitate the handling of raw materials and products.

A vertical retort can also be used for electrothermic reduction. In this case, the retort is normally 15 m high with an internal diameter of 2.4 m and produces about 100 tons of zinc per day. In the process used by St. Joe, electrodes of graphite are introduced through the silicon carbide walls at two places—near the bottom of the retort and at a zone about 9 m from the bottom. The charge in this zone forms the resistance and the electrical energy supplied provides the heat necessary for the reduction of the charge instead of the fossil fuel employed in conventional horizontal and vertical retorts.

The gas liberated due to the reduction of the charge contains 40-45 per cent Zn, 45 per cent CO2, 5-8 per cent H2, 5-10 per cent N2, and minute quantities of CO2. In the St. Joe process, this gas (i.e., zinc vapour) is bubbled through an U-tube arrangement whose exit is maintained under a vacuum to enable the suction of the retort gases through the molten zinc. The zinc condensation has to be carried out quickly in order to avoid the formation of the blue oxide of zinc (ZnO + Zn). In another process, namely, the New Jersey process, the zinc vapour is condensed in a splash zinc condenser.

The residues of the foregoing retort processes contain 3-4 per cent zinc, all the input iron, gangue, copper, and precious metals. The zinc recovery from these processes is over 95 per cent.

The zinc product obtained from the foregoing retort processes is known as spelter and contains other elements in addition to zinc. On melting, it forms three distinct layers, namely, a bottom layer of molten lead containing some zinc (about 1.5 per cent), a top layer of zinc containing some lead (about 0.8 per cent), and an intermediate layer of zinc and iron (15-20 per cent) called hard metal. The intermediate layer is recycled to the retorts and the lead layer is smelted in order to recover lead. The zinc layer is further refined by fractional distillation because the wide difference in the boiling points of Zn (907°C), Cd (780°C), and Pb (1620°C) facilitates the separation of one metal from the other.

Hydrometallurgical Extraction of Zinc

Hydrometallurgical processes have been used for the extraction of zinc from a wide variety of ores, including extremely low-grade ores. These processes not only yield zinc with a high degree of purity but they also lead to a higher rate of recovery of valuable byproducts than pyrometallurgical processes.

In a hydrometallurgical process, the zinc concentrate is first roasted in the same manner as in the retort process. In this case, however, a greater control is exercised over the roasting operation in order to minimize the formation of the ferrite ZnO·Fe2O3. As already mentioned, although this ferrite could be easily reduced, it was found to be virtually unleachable in the earlier hydrometallurgical processes, rendering it highly undesirable. This drawback has been overcome in the recently developed Jarosite and Goethite processes. The roasted zinc concentrate is dissolved in an acid and the valuable byproducts are precipitated out. The leach solution is finally electrolyzed for the recovery of zinc.

At present, ISP furnaces operate in the U.K., Zambia, France, Germany, Rumania, Japan and Canada. The construction of new units in other countries is under way.

Production of Other Metals by ISP

The ISP is well suited to the treatment of a wide variety of complex ores because it combines in one operation the recovery of the zinc metal and the lead bullion containing precious metals, copper, and other elements.

Lead Recovery
In the ISP, a considerable quantity of lead can be produced along with zinc. In this process, additional carbon is not required for reducing the lead. Experimental evidence has indicated that the maximum lead content of the feed sinter should be restricted to 28 per cent; otherwise, the operation becomes difficult, presumably due to the premature softening of the charge.

The capacity of a single furnace, with an area of 27 sq. m, at Avonmouth, U.K., is 100,000 tons of zinc and 75,000 tons of lead per year. At present, the total global annual zinc production by the ISP is about 1 million tons and the total global annual lead production about 0.5 million tons.

In the ISP furnace, molten lead is reduced in a zone high up in the shaft. As this lead falls through the charge, it collects the nonvolatile metals present in the charge (such as silver, gold, copper, antimony, and bismuth) so as to form the lead bullion. This bullion is ultimately tapped from the bottom of the furnace.

Cobalt

About three-fourths of the cobalt produced all over the world is used for metallurgical purposes (alloying) and one-fourth as oxides and other compounds in the ceramic and paint industries. Steels containing Co, Cr or Co, Cr, and W are used in the manufacture of cutting tools and dies. Often, the entire article is not made of the alloy, but only the surface is coated by a special process of hard facing. The alloys are also used for making surgical instruments, because of their inertness towards the human system. Co-Cr-Mo alloys are used in turbine blades because they possess extraordinary strength properties and, at high temperatures, offer excellent resistance to corrosion.

The mixed copper-cobalt ores of Zaire and Zambia form the largest source of cobalt. These ores occur both in the oxide and sulphide forms. The copper oxide ore which Contains 5-6 per cent Cu and 0.2-0.3 per cent Co is concentrated by flotation with palm oil, Na2CO3, and sodium silicate to yield a concentrate with 26-27 per cent Cu and 1 per cent Co at a Co recovery of 82-85 per cent. The oxide ores with 3.5 per cent Cu and 1.7 per cent Co are also concentrated by flotation to yield a concentrate with 10.4 per cent Cu and 7.9 per cent Co. The mixed sulphide-oxide ores contain 4-5 per cent Cu and 0.2-0.3 per cent Co. These ores are also concentrated by flotation with an alkaline sulphhydrate. In this case, a sulphide concentrate with 46 per cent Cu and 0.4-2.5 per cent Co and an oxide concentrate with 20 per cent Cu and 1.7 per cent Co is produced. The leach-electrowinning circuit adopted to extract copper and cobalt from their oxide concentrates is shown in Fig 1. The cobalt is essentially leached in an acid solution, precipitated after Cu removal, and the cobalt hydroxide fed to electrolytic cells to electrowin metallic cobalt.

The sulphide concentrates are first roasted in a fluid bed roaster at 675°C to produce soluble sulphates. Next, the sulphate calcine is leached with acid and the solute subjected to a process similar to that described for oxide concentrate leaching.

The sulphide and oxide nickel ores account for the second-largest source of cobalt. During the electrolytic refining of nickel, cobalt is precipitated as cobaltic hydroxide, which is subjected to leaching and then electrowinning in order to produce metallic cobalt.

Cobalt is also present in small amounts (0.1-0.2 per cent) in the slag discarded from nickel smelters and from some copper smelters. In these smelters, the converter slags are enriched in cobalt (0.4-1.0 per cent) and in some operations, these slags are reduced in an electric furance to produce an alloy containing 3-5 per cent Co with nickel, iron, copper, and sulphur constituting the remainder of the alloy. Cobalt is recovered from the alloy by conventional hydrometallurgical processing. During hydrometallurgical processing, solvent extraction, electrowinning, and hydrogen reduction steps are used.

Sodium

Production of Sodium

Sodium was first produced on a commercial scale towards the end of the nineteenth century. The process employed was the electrolytic decomposition of fused sodium hydroxide (Castner's process). This process was eventually superseded in the 1920's by the Downs process, which involved the electrolysis of fused sodium carbonate.
sodium chloride. The Downs process, which is still in use, accounts for an annual world production of nearly 200,000 tons.

The electrolytic process is entirely dependent on the availability of cheap electric power. Where power is not easily available or is prohibitively expensive, other methods have been attempted. Some of which are now mentioned.

Downs's Process

The most well-established process for the production of sodium, the Downs process, involves the electrolytic decomposition of sodium chloride. Since the principal and, indeed, the almost sole source of sodium in nature is common salt, it has a number of advantages over sodium hydroxide as the raw material. For example, common salt is considerably cheaper than sodium hydroxide and is also more readily purified and the electrolysis of the chloride produces a valuable byproduct, namely, chlorine. Consequently, earlier processes, such as Castner's process and Gilbert's process, which employed the electrolysis of the hydroxide, became obsolete. It should, however, be noted that the sodium chloride electrolysis suffers from certain drawbacks. For instance, the melting point of sodium chloride is high (804°C). Chloride-electrolysis, therefore, requires much higher operating-temperatures compared with hydroxide electrolysis which can be carried out at 310-320°C. The boiling point of sodium is also high (880°C). Consequently, the vapour pressure of sodium is quite high in the Downs cell, which operates at around 850°C. The vapours may readily burn in air (unless the cell design is suitably amended), leading to serious corrosion problems at high temperatures. Some of these drawbacks can be overcome as follows:

1. The liberated sodium may be dissolved in a molten cathode to form an alloy from which the metal may be recovered later by distillation or other methods.
2. The operating temperature may be lowered by using low melting eutectic mixtures (obtained by adding other more stable salts to sodium chloride).

Hydrochloric Acid

Hydrochloric acid is made (1) from common salt, in salt-cake furnaces and by the Hargreaves process; (2) by burning electrolytically produced chlorine in excess hydrogen; and (3) as a by-product from the chlorination of hydrocarbons such as pentane and benzene (C₆H₆ + Cl₂®C₆H₅Cl + HCl).

Hydrogen chloride is a gas; on cooling to room temperature, it does not condense to a liquid, as does nitric acid, but must be dissolved in water. The ordinary commercial strength is 200Bé, at 60°F (15.5°C), containing 32.46 per cent HCl. The system for absorption is essentially the same, whichever method is used for the production of hydrogen chloride. The basic differences lie in the method employed to purify the HCl vapor in preparation for absorption.

The heat generated in the absorption of HCl in water is considerable; it amounts to about 700 Btu per pound of HCl absorbed. In the absorption process described above, all of the heat is removed by water cooling on the first, or "absorber-cooler," tower.

Acid made by burning chlorine in hydrogen, with absorption in towers with iron-free packing, is water-white and essentially-chemically pure. It more than meets the requirements for the chemists C.P. acid.

Anhydrous hydrogen chloride is manufactured by passing hot gasses from the hydrogen-chlorine burner through anhydrous calcium chloride, which absorbs any water vapor present. The dry hydrogen chloride is then compressed and loaded into steel cylinders, special tank trucks, or tank cars.

The uses of hydrochloric acid include steel pickling (cleaning); the manufacture of dyes, phenol, and plastics; glucose and food processing; oil well acidizing; and a number of miscellaneous purposes requiring a strong and easily neutralized inorganic acid.

Sodium Hyposulfite (Hydrosulfite)

Sodium hyposulfite, anhydrous Na₂S₂O₄, called "hydrosulfite" in the trade, is a convenient form of the powerful reducer which is used principally for the reduction of vat dyes. Before its advent in the trade, it had
to be prepared as a solution in the textile mills and used at once. Formerly it had to be imported, chiefly
from Germany. There are now five manufacturers in the United States.

Caustic Soda and Chlorine

Caustic soda, NaOH, a white solid which is extremely soluble in water, has been made in the past by two
commercial processes: (1) causticizing soda ash with lime; and (2) by the electrolysis common salt, NaCl,
in water solution, with the simultaneous production of chlorine and hydrogen. Both processes date back to
the 19th century; lime-soda caustic was first marketed about 1850 and electrolytic caustic in 1892. Lime-
soda caustic dominated the market until 1940 when the increasing demand for chlorine caused the
coproduced electrolytic caustic to exceed lime-soda caustic production for the first time. The trend of a
relatively greater growth rate for chlorine than caustic has continued and, in 1968, forced the shutdown of
the last merchant lime-soda caustic plant.

Electrolysis of Brine

Many cells have been devised in which the decomposition of salt in water solution may be performed. The
commercially successful cells are of two basic types: diaphragm cells, and mercury cells. The first
percolating diaphragm cell was the LeSueur cell, from which evolved the Townsend, Allen-Moore, Nelson,
Gibbs, Vorce, Hooker, Dow Bi-polar, and other cells. The original mercury cell was the Castner, the
invention of an American.

For all cells it is customary to purify the salt solution and to use it as concentrated as possible, that is,
almost saturated, about 25 per cent NaCl. The manufacture of caustic soda in diaphragm cells, in a few
words, involves the preparation and purification of the saturated salt solution; electrolysis of this solution in
the cell, wherein half the salt is transformed into caustic; concentration of this mixed solution with
separation of the salt as the concentration rises; and finally evaporation to anhydrous caustic. For the
mercury cells, the procedure is about the same, except that the caustic liquor issuing from the cell is free
from salt. This is an important advantage if the liquor is to be used as produced, since it requires no
concentration. The liquor issuing from the diaphragm cell, with as much salt as caustic, could not be used
as such for most purposes. In the manufacture of solid caustic from diaphragm-cell liquor, a final product
containing 2 per cent salt is produced. This amount is not objectionable in many of the important
applications of caustic.

Purification of the Salt Solution

The salt may be in the form of a natural brine, an artificial brine, or rock salt. The purification of the latter
includes the same steps as those required for the brines. The salt is conveyed from hopper cars into an
underground hopper which feeds an inclined belt elevator, or bucket elevator, which raises the salt to the
dissolving tank. This is kept filled by pumping in warm water at the base and allowing it to overflow at the
top; during its passage through the salt the water becomes saturated. Instead of a wooden tank, a concrete
tower may be used. The brine is collected in the treating tank, where sodium carbonate and sodium
hydroxide are added in amounts just sufficient to precipitate the calcium and magnesium salts. After settling
to remove the coarser suspended particles, the brine is passed through sand or diatomaceous earth filters.
The filtered salt solution, containing about 25 per cent NaCl, is elevated to a tank above the cells and fed
through a constant-level boot to a pipe having side branch for each cell. The methods for regulating the
amount fed to the cell vary considerably; one of the simpler schemes is to insert a horizontal plate with a
small orifice in the vertical branch leading to the anode compartment, with a glass sleeve immediately
below the orifice-plate to permit observation of the flow. The size of the orifice determines the rate of flow.

Diaphragm Cells

All diaphragm cells embody the principle of enclosing the anode compartment with a diaphragm. However,
the modification in the construction of the later cells have been of the greatest importance; furthermore,
they differ from each other radically. One fundamental difference in cell design is the presence or absence
of liquor in the cathode compartment. The Hooker cell may be taken as typical of the diaphragm cells which have liquor in the cathode compartment.

The Hooker "S" Cell. The Hooker "S" cell (Fig. 2) is essentially square in cross section. It consists of a concrete top piece, a concrete bottom piece (set on short legs), and a central steel frame, which carries the iron-wire mesh forming the multifingered cathode. The latter is also the support for the asbestos diaphragm, an unbroken mat prepared by plunging the steel cathode into a suspension of asbestos fibers in cell liquor and applying suction to the cathode chamber. The anode is part of the bottom section. It is made of impregnated graphite slabs set in a bitumen-covered lead base plate which receives the current; the slabs reach up from below between the fingers of the cathode, so that every vertical face of the cathode and diaphragm is close to a similar graphite surface. A single broad-faced connection at the cathode of one cell carries the current the short distance to the single stout rod feeding the anode of the next cell. The construction will be clearer after examination of Fig. 2. The cell, closely packed as it is with anode and cathode branches, has a 4-inch central passage for anolyte circulation.

The brine is preheated to 60°C (140°F) and enters the cell in the dome (see sketch); the stream of brine breaks into drops, so that there is no electrical conductivity from the cell to pipes and heaters outside the cell. Its content of salt (NaCl) is 322 g per liter, essentially a saturated solution. The cell works at a temperature of 90°C (194°F). The chlorine-gas outlet is in the dome, a stoneware pipe connected to a larger stoneware header. The hydrogen leaves the upper level of the cathode chamber through an iron pipe, insulated by a rubber sleeve coupling. The caustic dribbles out from the lower part of cathode chamber through an adjustable outlet, so that the level of caustic in the chamber can be controlled.

Concentration of the Caustic Liquor

The liquor flowing from the cathode compartment of the diaphragm cells just discussed contains both caustic and salt. The solution contains 10 to 12 per cent NaOH and 14 to 16 per cent NaCl. It is concentrated in a triple-effect evaporator, for example, and each boiling pan may have its own separator in which the salt is collected as fast as it separates from solution, so that the heating surface in the pan may always be swept by liquor. When cell liquor has been concentrated to 50 per cent NaOH, only 1 per cent of salt remains in the solution. The salt in suspension is removed by settling and cooling, followed by a final filtration. The solid salt which is removed is redissolved in the evaporator condensate to make cell-feed brine. In some plants, the 50 per cent NaOH liquor is concentrated further to a 73 per cent concentration in a single vacuum pan heated with high-pressure steam. The liquid caustic, which is sold as such, offers several advantages: it may be handled in pipes; no drum containers are necessary; less labor and less fuel are required in its production in comparison with solid caustic; and it is in the form in which the customer applies it. In order to produce anhydrous caustic, the 50 or 73 per cent is boiled down in cast-iron pots heated by an oil or gas fire, until all the water is evaporated.

Liquid Chlorine

Shipping Liquid Chlorine. Liquid chlorine is shipped in 100 and 150 lb steel cylinders and in 1-ton steel containers 15 of which are placed on a specially equipped railroad flatcar. In addition to these containers which are usually purchased by consumers of small-amounts of chlorine, liquid chlorine is shipped in single-unit tank cars with capacities of 16, 30, 55, 85, and 90 net tons. Moreover, liquid chlorine is also shipped in barges along inland waterways. Such barges have capacities up to 640 net tons of liquid chlorine. A barge is equipped with four or six tanks to hold the chlorine. A recent innovation is the shipment of liquid chlorine by tank truck. This truck is of special design and has a carrying capacity of 16 net tons of liquid chlorine. Many chlorine-producing installations also pipe liquid or gaseous chlorine to other plant units for various chlorination operations. Pumps of special design are used in many installations to move liquid chlorine from one part of a plant to another.

The 1-ton unit is very convenient for making the bleach at a mill, such as a pulp mill, because once the
required quantity of milk of lime has been prepared, all the chlorine in the cylinder may be allowed to pass in without danger of wasting any. Calcium hypochlorite, Ca(OCl)2, and calcium chloride, CaC12, are formed. All containers have one or two internal pipes, so that either the gas or the liquid may be drawn. If the gas is drawn, heat must be supplied to make up for the heat of vaporization, or else the process is very slow. It is more convenient and simpler to use the liquid, mixing it directly with the milk of lime in a small mixing chamber, in that way the vaporization process uses part of the heat of reaction of the chlorine on the lime. This is important in keeping down the temperature of the mixture to prevent chlorate formation.

Hydrides of Boron

The isolation of the individual members by ingeneous manipulation methods was possible for the first time by Stock and his co-workers. The following list vide Table 1, includes all the well characterized boranes, there being in addition certain solid compounds which are possibly polymerised products.

Experimental Details- The apparatus consists of a flask F two litres in capacity, Fig. 1, provided with a mercury safety valve V. The mouth of a flask is fitted with a long cylindrical glass vessel provided with a vertical rod R which has lugs l1 and l2 etc. as can be observed from the diagram. The rod R can rotate by means of a motor attached to the wheel W. Magnesium boride is placed here and it slowly falls into the flask F through the opening O2; the rate being adjusted by the speed of rotation. Hydrogen passes from 0 and enters at O1 and travels down to O3 and enters the flask. Here the reaction between magnesium boride and hydrochloric acid (or preferably 8 Normal phosphoric acid) takes place. The mixture of hydrides of boron and hydrogen go up the condenser C where it is partially freed from water vapour. It now passes through the wash bottle B and then through the two U-tubes containing calcium chloride and phosphorus pentoxide respectively. The dry hydride is now cooled by liquid air at L and the individual hydrides separated by fractional condensation or by fractional distillation at low pressures.

Fractional Distillation- The material is condensed in a V-tube by the application of suitable low temperature and then the temperature is slowly raised under low pressure of the order of 1 mm. Connection to a second U-tube is made, when distillation takes place. All the material volatilizes at that temperature and pressure and is condensed in the second tube. The fraction obtained in the second tube is distilled into another U-tube by maintaining it at a certain temperature and pressure as in the previous cases. Thus the various hydrides are isolated.

It has been found that boron hydrides especially diborane and diborane monohalides can be synthesized by the reduction of boron halide vapour with hydrogen in the presence of metals at elevated temperatures. The apparatus consists of a reactor tube packed with a charge of aluminium, heated in a cylindrical furnace, followed by a trap to collect aluminium chloride formed during the reaction and by taps at -80°C and -190°C to collect the reaction products as shown in Fig. 2. The boron chloride and hydrogen are passed through the bottom at B, the reaction temperature is followed by a thermocouple imbeded in the charge of aluminium. On distillation of the condensed products following a run, it was observed that the material in the trap at -190°C is mostly diborane together with some hydrogen chloride. The greater portion of the boron hydride is collected at -80°C as diborane monochloride with excess of boron trichloride. Reduction with Metal Hydrides- It has been discovered recently that hydrides of alkali and alkaline earth metals will reduce gaseous boron hydrides to diborane at temperatures above 2000°C. A charge of powdered sodium hydride is placed in an inclined 1 inch pyrex tube and a mixture of boron fluoride and hydrogen in the ratio of 1:2 is passed through the charge while the temperature is gradually increased. At 180°C, considerable quantities of diborane are formed.

Oxyacids of Boron

Orthoboric Acid, H3BO3

Preparation: (1) From Borax-Orthoboric acid can be conveniently prepared by extracting one part of borax with four parts of boiling water and adding one third the quantity of sulphuric acid. On cooling the boric acid crystallizes.
crystals are deposited. The mother liquor is further concentrated and cooled to obtain a second batch of crystals. It can also be obtained by decomposing a solution of borax with hydrochloric acid and evaporating to dryness at 100°C. It is associated with sodium chloride, which is carefully removed by least possible quantity of water.

Properties

Crystals of boric acid are lustrous, colourless, flexible, with a greasy touch and six-sided plates sp. gr. 1.5 and melting point 184°-186°C. When heated to 100°C, it looses water and forms metaboric acid; at 140°C pyroboric acid is formed; finally at red-heat all water is lost and boric oxide is obtained.

\[
\begin{align*}
2\text{H}_3\text{BO}_3 & \rightarrow 2\text{H}_2\text{O} + 2\text{HBO}_2 \\
4 \text{HBO}_2 & \rightarrow \text{H}_2\text{O} + \text{H}_2\text{B}_4\text{O}_7 \\
\text{H}_2\text{B}_4\text{O}_7 & \rightarrow \text{H}_2\text{O} + 2\text{B}_2\text{O}_3
\end{align*}
\]

Properties

Borox is a white solid, crystalline and soluble in water, the solution being alkaline due to the formation of sodium hydroxide:

\[
\text{Na}_2\text{B}_4\text{O}_7 + 7\text{H}_2\text{O} \rightarrow 2\text{NaOH} + 4\text{H}_3\text{BO}_3
\]

Glycerine is said to retard the reaction. When heated, borax loses water of crystallization and swells up to a white porous mass. On heating further it melts into a clear transparent glass, which dissolves in metallic oxides to form coloured glasses. The borax bead test is based on this principle.

Perboric Acid and Perborates

The existence of perborates was first reported by Etard in 1880. He obtained barium perborate by mixing concentrated solutions of boric acid and barium peroxide. The perboric acid itself has not been isolated free in nature. Sodium perborate is an ideal compound belonging to this class. But later investigators differ in their views. When a solution of perborate is gently distilled under pressure at about 60°C, no water is formed in the distillate, but the percentage of active oxygen in the residue increases which is determined by titrating the acid solution with potassium permanganate and this is said to be about, 10.4 per cent. Thus it may be inferred that the active oxygen cannot be represented by, \text{H}_2\text{O}_2, of crystallization and hence the following constitution is recommended.

This is confirmed by the behaviour of potassium hypoborate, \text{KBO}_4\cdot\text{H}_2\text{O}, which evolves only traces of oxygen dissolved in water and on drying over phosphorus pentoxide in vacuo, a product having the formula, \text{4KBO}_4\cdot\text{H}_2\text{O}, is obtained. Hence this compound cannot be formulated as, \text{KBO}_3\cdot\text{H}_2\text{O}_2. Further this compound is stable but the other one, \text{KO.O.OBO}, is very unstable.

Sulfuric Acid

Sulfuric acid, a strong acid, is an oily, viscous, water-white, nonvolatile liquid. It absorbs water from the atmosphere. A drop of it on the skin causes a severe burn. It is made in large volume by the chemical industry. It is used as a solvent, a dehydrating agent, a reagent in chemical reactions or processes, an acid, a catalyst, an absorbent, etc. The concentrated acid is usually stored in steel tanks. The dilute acid may be stored in lead-lined or plastic tanks. It is used in very dilute concentrations and as strong fuming acid. It is often recovered and re-used. After use in some phases of the explosives, petroleum, and dye industries it is often recovered in a form unsuitable for re-use in that industry but suitable for use in another industry. It is a versatile, useful acid and has been called the "work horse" of the chemical industry.

The Manufacture of Sulfuric Acid

\textit{History}. Sulfuric acid is formed in nature by the oxidation and chemical decomposition of naturally occurring sulfur and sulfur-containing compounds. It is formed by the weathering of coal brasses or iron disulfide, discarded on refuse dumps at coal mines. It is formed by bacteria in hot sulfur springs. It is formed in the atmosphere by the oxidation of sulfur dioxide emitted from the combustion or coal, oil, and other substances. It is formed by chemical decomposition resulting from geological changes.
In ancient times sulfuric acid was probably made by distilling niter (potassium nitrate) and green vitriol (ferrous sulfate heptahydrate). Weathered iron pyrites were usually the source of the green vitriol. About 1740, the acid was made in England by burning sulfur in the presence of saltpeter (potassium nitrate) in a glass balloon flask. The vapors united with water to form acid which condensed on the walls of the flask. In 1746 the glass balloon flask was replaced by a large lead-lined box or chamber, giving rise to the name "chamber process." In 1827 Gay-Lussac, and in 1859 Glover, changed the circulation of gases in the plant by adding towers which are now known as Gay-Lussac and Glover towers. These permit the recovery from the exit gases of nitrogen oxides which are essential to the economic production of chamber acid. Today, most sulfuric acid made is produced by the contact process, based on scientific technology developed about 1900 and thereafter.

BASF built a successfully operating contact plant in 1898. General Chemical erected a pyrite-burning contact plant using the Herreshoff furnace.

The Chamber Process for Making Sulfuric Acid

The chamber process for making sulfuric acid, at first glance, appears to be a rather simple process requiring simple equipment. The reactions involved, however, are not simple and even today there is disagreement among experts as to just what does take place in the chambers. All agree, however, that the oxidation of sulfur dioxide to sulfuric acid in the chambers is not directly effected by oxygen but that intermediate compounds involving nitrogen oxides are formed and that the reaction is really a cyclic process involving the alternate formation and decomposition of the intermediate compounds. Many operators say that "operation of a chamber plant is more an art than a science."

The Contact Process

The basic features of the contact process for making sulfuric acid, as practiced today, were described in a patent issued in England in 1831. It disclosed that if sulfur dioxide, mixed with oxygen or air, is passed over heated platinum the sulfur dioxide is rapidly converted to sulfur trioxide, which can be dissolved in water to make sulfuric acid. The practical application of this disclosure, however, was delayed. An understanding of the complex reactions occurring in the gas phase over the catalyst required the development of that branch of physical chemistry known as chemical kinetics, and also the development of that branch of engineering known as chemical engineering. A demand for acid stronger than that which could be produced readily by the chamber process stimulated this development. The success of this process for making sulfuric acid led to the development of other catalytic processes for making many of the synthetic chemicals known today.

Nitric Acid

Nitric acid has been known since the 13th century. Glauber devised its synthesis from strong sulfuric acid and sodium nitrate; however, it was Lavoisier who showed that nitric acid contained oxygen; and Cavendish who showed that it could be made from moist air by an electric spark.

In the oldest methods used, Chile saltpeter was reacted with concentrated sulfuric acid in heated cast iron retorts; the evolved nitric-acid vapors were condensed and collected in stone-ware vessels.

Today nitric acid is made by oxidation of ammonia with air over a precious-metal catalyst at atmospheric or higher pressures and at 800 to 950°C. Nitric oxide is formed according to the reaction: \(2\text{NH}_3 + \frac{5}{2}\text{O}_2 = 2\text{NO} + 3\text{H}_2\text{O}\). The nitric oxide is then further oxidized by additional air to give \(2\text{NO}_2\), which combines with water to give \(\text{HNO}_3\) and nitric oxide. The nitric acid processes currently in use are listed in Table 1.

Pressures vary from atmospheric to 120 psig. The concentration of nitric acid that can be produced with conventional equipment is about 60 per cent. If higher strengths are needed, a special method of concentration is required.

Nitric acid can also be produced by the high-temperature combination of nitrogen with oxygen in the air, and by use of radiation. One method which has received considerable attention is the so-called "Wisconsin" process. Although a 40-ton per day plant was built, it could not compete economically with the conventional
ammonia-oxidation route.

Nitric acid is generally a light-amber liquid; however, the pure acid is colorless, strongly hygroscopic, and corrosive. It is a strong oxidizing acid. It boils at 78.2°C, freezes at -47°C, and forms a constant boiling mixture with water (68 per cent nitric acid by weight) which boils at approximately 122°C at atmospheric pressure. White fuming nitric acid usually contains 90 to 99 per cent by weight HNO₃, from 0 to 2 per cent by weight NO₂ and up to 10 per cent by weight water. Red fuming acid usually contains about 70 to 90 per cent by weight HNO₃, 2 to 25 per cent by weight NO₂, and up to 10 per cent by weight water.

The catalyst generally used for ammonia oxidation is a platinum-rhodium alloy containing about 10 per cent rhodium. A gauze made of wire 0.003 inch in diameter with about 80 meshes to the inch is used. During the life of the catalyst it becomes polycrystalline in appearance. There is also some weight loss, the effect of which is more pronounced at the higher converter temperatures employed in the pressure process. With the atmospheric processes at lower temperature the platinum loss is about 45 mg per metric ton of acid produced. Recovery steps are required for operation at 120-pound pressure. This usually involves periodic cleaning of the converter and heat exchange equipment, and the use of a filter in the gas stream beyond these pieces of equipment.

There are a number of materials which will catalyze the oxidation of ammonia. Platinum modified with other metals has been generally accepted. Recently, innovations have been introduced. Engelhard Industries has offered a Random Pack catalyst that uses 60 per cent less platinum and is offered along with a "getter" which will capture the volatilized platinum. Another new catalyst is offered by C & I Girdler, Inc. This is not a noble metal catalyst according to trade sources. Yields are reported to be 93 to 94 per cent after two years, whereas the standard platinum catalyst yield drops from 98 to 91 per cent over a six-weeks period. I.C.I. in England has also developed a new nonplatinum or nonprecious metal catalyst and the yield is as high as for other catalysts.

Absorption of nitric oxide takes place in a bubble-cap tower into which air is added to oxidize the nitric oxide to nitrogen dioxide. The nitrogen dioxide must be absorbed in water to liberate nitric acid and nitric oxide. There are two equilibria as follows: N₂O₄ = 2NO₂ = 2NO + O₂. The first of these two equilibria is established relatively quickly; the second more slowly. At 150°C the nitrogen tetroxide is almost completely decomposed into nitrogen dioxide. At 500°C the equilibria lies at 25 per cent nitrogen dioxide and 75 per cent nitric oxide. The formation of nitrogen dioxide from nitric oxide and oxygen is relatively slow at atmospheric pressure, but proceeds quite rapidly under higher pressure. It is interesting to note that this reaction has a negative temperature coefficient. The absorber is usually operated at the lowest temperature obtainable with available cooling water, in the temperature range of 10 to 40°C.

The absorption characteristics of nitrogen dioxide in water are of importance in the design of the absorber. There are two factors which determine the strength of the nitric acid in the absorption tower, namely, total pressure on the system and gas composition. To increase by 10 per cent the strength of nitric acid in equilibrium with a gas of fixed composition it is necessary to raise the pressure about ten fold.

Atmospheric oxidation enhances this possibility. The remaining nitric oxide is oxidized to nitrogen dioxide, which is oxidized to nitric acid with high purity oxygen in the autoclave at about 60-80°C and 50 Kp/cm² gage.

As a result, pressures will build up in storage vessels. Nitric acid is also very corrosive, and some stabilizers or corrosion inhibitors are also used.

Corrosion of aluminum by red fuming nitric acid is reduced by adding 4 per cent by weight of hydrogen fluoride (52 per cent HF).

Decomposition of the concentrated acid is reduced by such substances as quaternary ammonium compounds, organic sulfones, inorganic persulfates, and organic sulfonium compounds.

Pollution Abatement. The tail gas from ammonia-oxidation processes will usually contain sufficient nitrogen
oxides to result in serious atmospheric pollution (smog) or in serious corrosion of power recovery-equipment, if such is used, unless some means for removal of the oxide is employed. The oxides are usually reduced with natural gas, hydrogen, or a carbon monoxide-containing gas, or they can be absorbed by alkaline liquors (soda, calcium, or magnesium) or ammonium sulfite-bisulfite.

**Hexamethylenetetramine**

The reaction mixture is controlled at a pH of 7 to 8 at a temperature of 30 to 50°C. Under acidic conditions, formic acid, carbon dioxide, and water are produced. At temperatures above 50°C decomposition of the tetramine occurs. Tetramine is produced either by continuous or batch operation. In batch operation, cycle times up to 6 to 8 hours have been used, whereas in continuous operation the holdup may be only 15 to 30 minutes.

Figure 1 shows the equipment which is used in the process. Thirty-seven per cent formaldehyde, usually containing less than 2 per cent methanol, is fed, together with ammonia; to a reactor which is cooled as a result of the solution being circulated through a water-cooled heat exchanger. The effluent from the reactor is fed to a vacuum evaporator. Here the product is concentrated, and crystals are formed. The slurry is centrifuged, and the crystals are washed and discharged to a drier. The mother liquor is recycled to the reaction system; however, a small bleed is necessary to avoid the build-up of impurities in the system. The mechanism of the reaction is discussed. They indicate a one-step trimerization reaction of the third order in which the rate is proportional to the ammonia concentration and the square of the formaldehyde concentration. Others have indicated a more complex reaction mechanism. The exact mechanism may depend on whether ammonia or formaldehyde is in excess.

The reaction may be carried out at temperatures up to about 50°C. Above this temperature the rate of hexamine decomposition becomes excessive. The degree of conversion is essentially complete after 4 or 5 hours; only minor benefits are obtained by operating for 6 to 8 hours.

The vessels are usually made of stainless steel or aluminum. The heat exchanger for cooling the reaction mixtures is also made of stainless. Crystallization takes place in the evaporator, and it is important to note at this point that hexamine has an inverse solubility. At 25°C, 86.7 grams are dissolved in 100 cubic centimeters of water, whereas at 50°C the solubility is only 80 grams per 100 cubic centimeters of water. The continuous addition of a small amount of ammonia during the evaporation step tends to reduce the decomposition of the tetramine during evaporation. If the formaldehyde feed contains methanol, it will be removed from the system along with the ammonia and water from the evaporator. The evaporators are usually made of stainless steel.

In the final drying step the temperature must be held to less than 50°C to avoid decomposition. The over-all yield is good, on the order of 95 to 96 per cent based on the formaldehyde.

Hexamine is used in the production of high explosives. The manufacture of "RDX" came into its own during World War II. By nitrating hexamine, a compound with high explosive properties is obtained. Hexamine is also used in thermosetting resin production as a curing agent. This is its principal use in a peacetime economy. It serves as a methylating agent in the curing of phenol-formaldehyde resins. The hexamine produces methylene groups without forming water, as is the case with paraformaldehyde. It is used as an accelerator in the rubber industry to prevent vulcanized rubber from blocking. Pharmaceutical applications exist for hexamine and some of its derivatives. It is also being studied as a fungicide in the citrus fruit industry as an inhibitor of corrosion caused by strong mineral acids, as a shrink-proofing agent in the textile industry, and as an agent to improve color fastness and to give better elasticity to cellulosic fibers.

**Hydrogen Cyanide**

Hydrogen cyanide is a relatively new commercial chemical. It is increasing in importance with the rapid growth of methyl methacrylate, acrylonitrile, and other chemicals. Ordinarily hydrogen cyanide is a gas, and it is a very toxic material. It has a melting point of -14°C and can be liquefied by cooling to 26°C. The liquid...
is colorless. It is soluble in cold water, alcohol, and ether. It forms explosive mixtures with air. The lower limit of flammability is 5.6 per cent, and the upper limit is 40 per cent.

As of October 1, 1967, the estimated annual capacity for HCN was 185,000 tons, excluding some internal commercial consumptions, such as in the manufacture of adiponitrile and ferrocyanide pigments. Over the years 1956 to 1966, the growth rate was 3.5 per cent per year. Future growth will partly depend on the use in chelates for detergent manufacture.

Sodium cyanide can be manufactured in several ways. One of the earliest methods involves the action of sulfuric acid on sodium cyanide, a process which is convenient for small quantities. Sodium cyanide may also be produced by reacting sodium carbonate with carbon and nitrogen, or by reacting sodamide with charcoal, or by passing ammonia and carbon monoxide through molten sodium to form a mixture sodium cyanide and carbon dioxide.

Hydrogen cyanide may be obtained from hydrogen, nitrogen, and carbon by passing the two gases through an electric arc formed by two carbon electrodes. The conversion is low even at 2,000°C, hence the reaction is not of commercial importance.

Formamide has been dehydrated to produce hydrogen cyanide and water. Today, however, most hydrogen cyanide is produced by the reaction of ammonia with methane and air (Fig. 1). Since the reaction will proceed only if sufficient heat is supplied, the air is used to burn the methane and produce the heat required. The reaction of methane with ammonia is as follows:

\[ \text{CH}_4 + \text{NH}_3 \rightarrow \text{HCN} + 3\text{H}_2 \]

The formation of hydrogen cyanide requires the addition of heat-60 kilocalories per mole. In some instances the heat is supplied to the reaction zone through small-diameter converter tubes, in which case the converter gases are not diluted with large volumes of nitrogen from the air.

A catalyst is universally employed. A platinum catalyst may be used. However, it is usually alloyed with 10 to 20 per cent rhodium and deposited on a ceramic material to give it mechanical strength, or it may be used as a gauze.

Under conditions of hydrogen cyanide synthesis, platinum alone will volatilize, and in some cases recrystallize. Both these phenomena will result in the loss of catalyst. When alloyed with rhodium, the catalyst will give satisfactory performance for as long as 4,000 hours.

In many cases the converters are provided with rupture discs to relieve the pressures which may result from explosions caused by improper control of feed materials.

Ordinarily the converter is started by heating a portion of the gauze electrically, or with a torch, to reach reaction temperature. The reaction then spreads throughout the gauze as a result of the overall exothermic reaction.

Approximately 60 to 67 per cent ammonia and 53 per cent methane are converted in a single pass. Higher conversions may be obtained at pressures of 30 to 40 psig. The choice of pressure is influenced more by the recovery system than by the advantages to be gained in the synthesis step.

It is important that the reaction mixture be cooled quickly to avoid cracking the hydrogen cyanide. Basic materials, such as ammonia promote polymerization. Accordingly, the gases are introduced into a waste-heat boiler where about 6 pounds of steam are produced per pound of hydrogen cyanide. From the waste-heat boiler the gases are passed through a cooler and then to an ammonia absorption system. At this point in the process several innovations have been developed. The most common method for removing ammonia is to use sulfuric acid as the absorbent. However, a polyhydroxy-boric acid complex, which is also used, has one advantage the ammonia may be recovered for recycle. The bottoms from the scrubbing tower contain an aqueous ammonium sulfate, which is processed further to produce solid ammonium sulfate. The over head gases which are free from ammonia are then absorbed in water prior to purification. The water-hydrogen cyanide mixture is rectified in a final scrubber to produce 99 per cent hydrogen cyanide.
Materials selection is important in the construction of the equipment. Aluminum has good corrosion resistance to the reaction products but it lacks strength above 600°C, and it promotes polymerization of hydrogen cyanide in the presence of ammonia and moisture.

Phosphorus

Manufacture of Red Phosphorus

A diagrammatic representation of the plant used for the manufacture of red phosphorus is given in Fig. 3. It consists of a massive iron pot provided with an upright pipe known as iron safety tube. Inside the iron pot, yellow phosphorus is placed. The thermometers on the sides record the temperatures, this is about 240º to 250ºC. The iron pot is heated in a coke furnace built of fire-brick. Great care is to be taken not to increase the temperature beyond 260ºC. Since the transformation of white phosphorus to red is exothermic, any increase of temperature above 260ºC may cause the whole of the phosphorus to vaporize suddenly, and cause the pot to burst. Hence the pot is provided with a safety valve. The resulting mass is hard and contains some yellow phosphorus. It is powdered, and boiled with sodium hydroxide to remove any yellow phosphorus. The residue is finally washed and dried. It consists of 99.5 per cent red phosphorus.

Latest Method-A continuous process for the formation of red phosphorus has been recently developed by the laboratories of Tennessee Valley which shortens the time required for processing white phosphorus from days to hours. Liquid white phosphorus is maintained at its boiling point in a reaction vessel with a retention period of 5 to 6 hours, thereby converting 35 to 50 per cent of white phosphorus to solid red phosphorus. The resulting slurry overflows continuously into a heated screw conveyer in which it is carried counter current to a stream of hot inert gas. The white phosphorus is now vapourized and then carried to a condenser to be collected and recrystallized. The red phosphorus is discharged in the form of fine particles whose size can be controlled to a considerable degree. This process neither requires treatment with boiling caustic nor grinding as in the batch process. Further this process yields a product of high purity, needed for certain industrial applications.

Manufacture of Phosphorus in India-The present day requirements of red phosphorus for Indian industries and non-ferrous metallurgy is about 200-250 tons per annum. Considering the expansion of match industry, the development of non-ferrous metallurgy and the operational economics, it has been considered that a plant producing almost a ton of red phosphorus daily would suffice the need of this country.

Hydrides of Phosphorus

Phosphorus forms the following hydrides.

1. Phosphorus Trihydride or Phosphine, PH₃.
3. Hydrogen diphosphide, P₂H.

Other Hydrides of Phosphorus

Hydrogen hemienneaphosphide, P₉H₂ is formed when the diphosphide is warmed at 170ºC.

₅P₁₂H₆ ® ₆P₉H₂ + ₆PH₃.

When alkali phosphides of the type, M₂P₅, are treated with dilute acetic acid, hydrogen hemipentaphosphide, H₂P₅, is formed.

Industrial Applications

Phosphorus pentoxide is used (1) As a desiccating or drying agent, and (2) For preparing phosphoric acid.

Structure

Phosphorus pentoxide, P₄O₁₀, may be represented as follows:

H. Henstock gave the following electronic structure to phosphorus pentoxide.

The modern structure of P₂O₅ is given below.

Tin

Concentration of Tin Ores
Cassiterite (SnO₂) is by far the most important mineral of tin. It is found mainly in Bolivia, Malaysia, and Indonesia. In India, no significant tin deposits have yet been located. Naturally occurring cassiterite is usually associated with the gangue materials and metallic sulphides such as galena, chalcopyrite, iron pyrite, and sphalerite. The theoretical tin content of SnO₂ is 78.6 per cent. In reality, however, ores may contain as little as 1 per cent tin or even less. To upgrade these ores to about 65 per cent tin, the water gravity concentration methods are employed. During such upgrading the gangue is removed, but since the specific gravities of the other metal sulphides are almost the same as that of cassiterite, they cannot be eliminated by ordinary gravity methods. Flotation methods have also not been successful so far in separating the tin mineral from other minerals. Iron- and tungsten-bearing materials, if present with tin ores, are separated by magnetic roasting and subsequent magnetic separation.

Rotary Furnace Smelting
The rotary furnace smelting of tin concentrates is gradually replacing reverberatory furnace smelting because it can achieve a higher efficiency of tin recovery (see Davey and Wills, 1977, 1978). In rotary furnace smelting, after the first smelting, the slag produced is reduced, and the tin is volatilized either in the form of SnS (when sufficient sulphur is present) or in the form of SnO (in the absence of sufficient sulphur). The tin-rich fumes are transported to the first smelting stage, and the cleaned slag produced after reduction is discarded. It may be noted that the vapour pressure of SnS is of an order of magnitude higher than that of SnO and the presence of SO₂ is beneficial to tin volatilization.

There is a proposal to employ volatilization to upgrade low-grade tin ores. Upgrading produces tin-rich fumes which are used as the feed in the existing type of smelter, which is capable of treating only high-grade concentrates.

Refining of Tin
There are two methods of refining tin, namely, pyrometallurgical refining (or fire refining) and electrolytic refining.

Electrolytic Refining of Tin
Recent research has developed a viable process for the electrolytic refining of tin. This process, which employs a mixture of sulphuric acid and phenol sulphonic acid as the electrolyte, is feasible especially if the tin contains a large amount of impurities such as Pb, Bi, Sb, and As. Another process, which uses a mixture of cresol sulphonic acid and phenol sulphonic acid as the electrolyte, is in the development stage.

The electrolytic bath contains stannous sulphate, cresol sulphonic acid and phenol sulphonic acid (to improve the conductivity of the electrolyte) and free sulphonic acid with b-naphthol and glue as addition agents. (Addition agents are necessary to prevent tree-like dendritic deposits on the cathode which may short-circuit the cell.)

The cell operates at room temperature at a cell voltage of 0.3 and a current efficiency of 85 per cent. Anodes made of the impure metal, which analyze about 95 per cent Sn dissolve in about 21 days, whereas the pure metal cathode sheets are withdrawn once every week. If the lead content of the anode is high, the slimes which fall from the anode are excessive and have to be removed frequently. Further, other slimes sticking to the anode are scrubbed off with revolving brushes so as to provide a smooth flow of electricity to ensure a high current efficiency.

The high purity tin obtained as a result of electrolysis typically analyzes (wt %) Sn, 99.95; Sb, 0.02; As, 0.01; Bi, 0.01; Cd, 0.01; Cu, 0.001; Fe, 0.01; Ph,0.02; (Ni + Co), 0.01; S,0.01; and Zn, 0.005.

Ferroalloys
It should be noted that single ferroalloy may perform more than one function depending on factors such as the composition and the condition of the molten steel, and the amount of ferroalloy used. Some complex ferroalloys have recently brought about improvements in both mechanical properties and chemical refining which are not readily achieved by several alloys used individually.
General Methods of Producing Ferroalloys

The basic steps in the production of ferroalloys are ore beneficiation, reduction, and refining.

Beneficiation

To produce ferroalloys on a commercially viable basis, it is necessary to ensure that the metal content in an ore is high compared with the iron content. The main purpose of beneficiation is to increase the metal content in lean ores. The principal methods of beneficiation fall into two categories, namely, physical methods such as washing, gravity separation, and magnetic separation and chemical methods such as acid leaching and roasting.

In India, some groundwork has been done with regard to the beneficiation of the Indigenous ores of ferroalloying elements. Table 2 summarizes some of the typical beneficiation techniques employed in India.

Ferroalloys are generally produced from the beneficiated ore by two processes, namely, carbon reduction and metallothermic reduction.

In the first process, suitable minerals mixed with iron ore are reduced by coke to produce high-carbon ferroalloys. The carbon content of these ferroalloys may be lowered by subsequent refining techniques. The carbothermic reduction and the subsequent refining operations, which require high temperatures, are mostly carried out in an electric furnace. Ferromanganese can be produced also in a blast furnace.

In the metallothermic reduction method, commonly referred to as the Goldschmidt process, oxide ores are reduced by aluminium in the presence of scrap iron to yield ferroalloys. This method is suitable for the production of alloys without carbon and for operation on a small scale. Aluminothermic reduction is an exothermic process, and, in most cases, is autogenous and does not require external heating.

We now discuss carbon reduction and aluminothermic reduction in detail.

Refining of Ferroalloys

The main purpose of refining a ferroalloy produced by carbothermic reduction is to lower its carbon content. The methods generally employed are:

1. The removal by oxidation. This involves
   a. the treatment of alloy by oxidizing slags,
   b. the controlled oxidation of carbon by oxygen,
   c. the oxidation of carbon under vacuum.
2. The removal of carbon by the introduction of an element into the molten alloy in order to decrease the solubility of carbon in the alloy.

We now give examples of ferroalloy refining.

In the production of ferromanganese, a high-carbon ferromanganese (7 per cent carbon) is first produced. To obtain a medium-carbon ferromanganese (2 per cent carbon), the high-carbon ferromanganese is initially smelted along with fresh manganese ore and a manganese-rich slag (20-40 per cent manganese). Next, a part of the carbon in the high-carbon ferromanganese is oxidized by the manganese dioxide in the fresh ore to yield medium-carbon ferromanganese. To obtain a low-carbon ferromanganese, the manganese-rich slag is once again smelted along with carbon to produce silicomanganese and a slag with a low manganese content (2-8 per cent manganese) which can be discarded. (Silicomanganese does not contain any carbon because silicon decreases the solubility of carbon and also because the silicide is more stable than the carbide.) When silicomanganese is smelted with sufficient fresh manganese ore to oxidize only the silicon, low-carbon ferromanganese (0.5 per cent carbon) is produced. We thus conclude that, in ferromanganese production, the principle of oxidation using oxidizing slags and that of decreasing the solubility of carbon by introducing another element form the basis for the production of medium- and low-carbon ferromanganese.

In the case of ferrochromium, a low-carbon ferrochromium is obtained from a high-carbon ferrochromium by applying the principle of the controlled oxidation of carbon with oxygen in the presence of an inert gas or...
under vacuum. The relevant reactions are

\[3\text{Cr} + 2\text{O}_2 (g) = \text{Cr}_3\text{O}_4,\]
\[4\text{C} + \text{Cr}_3\text{O}_4 = 3\text{Cr} + 4\text{CO} (g),\]

where C and Cr denote, respectively, carbon and chromium dissolved in the ferroalloy. If reaction (6.70b) is made to proceed towards the right, carbon can be removed without oxidizing the chromium from the ferroalloy. The thermodynamics of reaction (6.70b) shows that at high temperatures (>1500°C), the removal of carbon is favoured. Also, it is clear from reaction (6.70b) that decarburization is favoured when the partial pressure of CO is lowered. This lowering can be achieved either by vacuum or by inert gas (argon) purging. Presently, both techniques, namely, vacuum oxygen decarburization (VOD) and argon oxygen decarburization (AOD), are widely employed in the manufacture of stainless steels, which are mainly Fe-Cr alloys.

### Manganese

#### Electrolytic Manganese

In the aqueous electrolysis of manganese, a diaphragm cell is necessary to control the pH in the anode and the cathode compartments. The pH must be controlled in order to suppress the evolution of hydrogen at the high voltage needed for depositing manganese on the cathode. It should be borne in mind that at such a high voltage, in an acid solution, hydrogen is evolved before manganese can be deposited.

The operating conditions are as follows:

**Purified solution (feed to electrolysis)**

- Mn (as MnSO₄) 30-40 gm/litre
- \((\text{NH}_4)\text{SO}_4\) 125-150 gm/litre
- SO₂ 0.01 gm/litre
- Glue 0.008-0.016 gm/litre

**Anolyte**

- Mn (as MnSO₄) 10-20 gm/litre
- H₂SO₄ 25-40 gm/litre
- \((\text{NH}_4)\text{SO}_4\) 125-150 gm/litre

**Current density** 4-6 A/mm²

**Catholyte (pH)** 6-7.2

**Cell voltage** 5.1 V

**Current efficiency** 60-65 per cent

The manganese produced by electrolysis is 99.94 per cent pure. The main impurities are hydrogen (0.015 per cent) and sulphur (0.04 per cent). Hydrogen is removed by heating the metal to 500°C.

The purple solution of KMnO₄ obtained as above is filtered through asbestos, concentrated and allowed to crystallise when KMnO₄ deposits as deep purple-red rhombic prisms.

### Phosphoric Acid

#### Production of Elemental Phosphorus and Phosphoric Acid

Phosphate rock is converted into usable chemicals by two major methods: (1) the wet acid process which produces an impure phosphoric acid, and (2) the burning of elemental phosphorus to give a pure phosphoric acid suitable for use in food products and for the preparation of pure phosphates. Production of the elemental phosphorus uses an electric furnace. The wet-process acid can be purified to produce pure phosphates.

The furnace is fabricated from a carbon steel shell and cooled on the outside with water. The hearth and lower section of the interior walls are fabricated of monolithic carbon and the upper section and roof are of zircon cement. Power is introduced through three electrodes, and because 40,000 to 60,000 KVA of power is needed, the power source is a three-phase system. Electrodes 48 to 60 inches in diameter are needed to
conduct the tremendous quantity of power required. The power flow through each phase is maintained about equal by a complicated system of raising or lowering electrodes to control their contact with the conducting fused mass. Control of power consumption from each phase is important to maintain a high power factor and thereby a minimum power cost.

Auxiliaries for the furnace include the equipment used to charge the furnace with raw materials, remove solids from the vapors from the furnace, condense phosphorus from the off-gas; and tap molten by-products from the furnace. These are also shown in Fig. 1. The charging equipment consists of weight belts, elevators, and charging chutes. The equipment is designed to insure a charge of constant composition to each chute. Solids are removed from the hot gases by use of an electrostatic precipitator consisting of a tube with a wire in the center to provide a positive and negative charge. Solids are electrically charged prior to entering the tubes and are removed by attraction to the opposite charge in the tubes, then emptied through the bottom of the tube. Phosphorus vapor and carbon monoxide pass from the top of the precipitator. The phosphorus is separated from other gases in a condenser equipped with water sprays directed at the gases to cool them. Carbon monoxide passes through the condenser. The liquid phosphorus and water flow by gravity to sumps and the phosphorus settles and is pumped to storage. Phosphorus-containing impurities are separated from pure phosphorus by differences in gravity and are subsequently handled in a separate system.

Industrial Phosphates
Phosphorus is essential to all animal and plant life. Phosphate salts play a major role in industrial processing and they have been major additives to detergents for household and industrial use. (They currently face severe restrictions as detergent additives because of their role in water pollution.) The metallic phosphates are an important group of chemicals but the sodium salts are in greater use because they are low cost and are especially effective in many applications. This discussion will be limited to a brief review of those salts which are produced from phosphoric acid and sodium compounds such as sodium carbonate and sodium hydroxide.

Classification. The commercial sodium phosphates might be classified in a general way as (1) orthophosphates, (2) crystalline condensed phosphates, and (3) glassy condensed phosphates. Monosodium and disodium orthophosphates are produced according to the following reactions:

Monosodium phosphate: $2\text{H}_3\text{PO}_4 + \text{Na}_2\text{CO}_3 \rightarrow 2\text{NaH}_2\text{PO}_4 + \text{H}_2\text{O} + \text{CO}_2$

Disodium phosphate: $\text{H}_3\text{PO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{Na}_2\text{HPO}_4 + \text{H}_2\text{O} + \text{CO}_2$

Trisodium phosphate ($\text{Na}_3\text{PO}_4$) cannot be produced by the addition of more sodium carbonate because the carbonate is not sufficiently basic. Sodium hydroxide must be used. The orthophosphates have a wide range of uses, but the production of condensed phosphates from them greatly extends their usefulness.

Wet-Process Phosphoric Acid
The materials then pass successively by gravity through a series of reactors. The temperature in the reactors is controlled by blowing air into them or by cooling the recycled slurry under vacuum in a separate flash cooler. The amount of slurry recycled varies from zero to a very large ratio of tons of $\text{P}_2\text{O}_5$ per ton of $\text{P}_2\text{O}_5$ introduced as rock. Recently, extremely high recycle ratios well above those usually in use have been shown to greatly increase plant capacity without decreasing extraction efficiency or product-acid concentration.

The slurry, except for that which is recycled from the last reactor, passes to a filter-feed tank from where it is introduced to the filter at a controlled rate. Modern filters are specially designed for the separation of gypsum from acid, proper washing of the cake to remove a maximum amount of acid, dumping the cake, and washing the filter cloth with water from underneath to remove cake from the perforations in the cloth.
Figure 6 is a flow diagram for the filtration of wet-process phosphoric acid. The cake, practically depleted of soluble P2O5, is finally washed with water at the end of the filter. Then in successive steps to the left and toward the front of the filter, washes are made in increasing concentrations of phosphoric acid. Most modern filters are divided into separate sections which are containers with their own filter cloths. Each section is under vacuum to pull liquid through the cake. The liquid is either recycled back to the cake on the filter, or to the reaction system, or separated as product acid.

The product acid contains from 28 to 35 per cent P2O5. The product is impure and precipitates form for several months. If used within a short time for the production of fertilizers, the potential precipitates decrease the P2O5 content of the product only slightly.

Some wet-process phosphoric acid is used for the production of ammonium phosphate or liquid fertilizers. In such uses it must be concentrated to about 40 per cent P2O5 for production of ammonium phosphates or 54 per cent P2O5 for liquid fertilizers. Concentration is usually made in a single-effect evaporator heated by steam with auxiliaries to control the formation of scales containing calcium sulfate. An evaporator may be in operation for about three days followed with a water wash of about one day. Unless some such schedule is followed, the tubes fill with scale to the extent that heat transfer is seriously decreased and cleaning becomes difficult. Accelerated cleaning is possible by washing the inside of the tubes with water at high pressure through specially designed nozzles. Sequestrants such as ethylenediaminetriacetic acid are also used as a wash, but this method is expensive.

Indium

In the hydrothermal stage of igneous activity, indium is concentrated in polymetallic ores, eg, sphalerite averages 1440 ppm and chalcopyrite 445 ppm of indium. Although the large pyritic base metal deposits contain only 18 ppm of indium (in their chalcopyrite constituent), in view of their huge size these deposits constitute an important potential source for indium. Concentrations of indium up to tenths of a percent have been found occasionally in some iron hydroxides. The indium content of sediments formed by geological supergene processes varies from 10-6 to 10-5%, argillaceous and sandy sediments containing more than carbonaceous sediments. The concentration of indium in ore bodies, though dependent on the primary ore-forming fluid and the conditions of deposition, appears very closely related to the tin content of host ores. Oxidized zinc minerals like smithsonite and goslarite contain ten to one hundred times less indium than the primary sphalerite. After examining hundreds of specimens of zinc, lead, silver, and gold ores, Murray and his colleague found a deposit of 35,000 tons of ore averaging 1.93 oz of indium per ton.

Indium has no ore of its own which is commercially exploitable. Like other rarer metals, it becomes concentrated in various by-products of metallurgical operations such as zinc residues and smelter slags from which it is feasible to recover indium commercially.

Methods of Manufacture

In the Anaconda process, the zinc calcine or blast furnace fume is stripped of its zinc oxide by a dilute sulfuric acid leach. The residue containing indium is dissolved in strong sulfuric acid. Indium is precipitated as the hydroxide or sulfite which is redissolved in acid and sulfuretted with hydrogen sulfide. Sponge indium is then produced by cementation with zinc and further purified electrolytically.

Two independent processes have been developed by Asarco. In the first, indium-containing residues are leached with strong acid and indium precipitated as a phosphate which is then treated with hot sodium hydroxide to obtain indium hydroxide. This hydroxide is reduced to the metal and further refined electrolytically. In the second method, a chloride slag obtained from a zinc-lead bullion is leached with dilute sulfuric acid and an indium-zinc sponge produced by addition of zinc dust. The sponge is further purified by chlorination followed by electrolysis.

The Rammelsberg ore processing involves leaching of a cupellation residue with dilute sulfuric acid. The solution is treated with zinc slabs to obtain crude indium sponge which is further dissolved in acid and...
indium of four-nine purity (99.99%) cemented by either aluminum strips or a zinc-indium-cadmium alloy.

Methods of Analysis

Any of the gravimetric or titrimetric procedures described earlier may also be applied to the analysis of indium compounds, without any prior separation.

The more common salts of indium, i.e., the halides, sulfate, and nitrate, are very soluble in water, while the hydroxides, sulfides, and oxides are easily soluble in dilute mineral acid. The halides, however, are extremely hygroscopic, and this fact should be borne in mind when weighing samples of these salts; weighing must be performed as rapidly as possible using a weighing bottle.

Procedure

Prepare a 0.03 M EDTA solution by dissolving 11.18 g of disodium ethyl-enediaminetetraacetate dihydrate in 1 liter of water. Prepare a 0.03 M cupric sulfate solution by dissolving 7.500 g of cupric sulfate pentahydrate in 1 liter of water. Prepare the PAN indicator solution by dissolving 0.1 g of 1-(2-pyridylazo)-2-naphthol (PAN) in 100 ml of 95% ethanol. Determine the titer of the cupric sulfate solution by titrating with the 0.03 M EDTA solution using PAN indicator solution. Then, mix equivalent amounts of the copper and EDTA solutions as ascertained by the titration. Prepare 50 ml of this solution which is stable for an indefinite period of time.

Molybdenum

The use of molybdenum as ferromolybdenum has been discussed in Chapter 6. Molybdenum occurs mainly as molybdenite (MoS2) in disseminated porphyry deposits. They are characterized by their low grade and large volume. In these deposits, the molybdenum content varies from 0.1 per cent to 0.5 per cent, and the ore is associated with pyrite and small amounts of tungsten, tin, topaz, and uranium (brannerite). Molybdenite also occurs in some copper porphyry deposits, but its content is low at 0.005 per cent to 0.1 per cent. Nevertheless, the copper porphyry deposits presently account for over 40 per cent of the world's molybdenum production.

In the extraction process, the molybdenite in the ore is concentrated by flotation because it possesses excellent flotation characteristics. A comparison of the contact angle measurements of common sulphide minerals given in table 1 shows that MoS2 has a higher flotation capability than other common sulphide minerals.

Because of the excellent flotability of molybdenite, it is possible to float it with hydrocarbon addition, and the addition of xanthate or thiophosphate is not necessary.

From molybdenum porphyry ores, over 90 per cent of the molybdenum can be recovered by comminution and flotation in a concentrate containing over 90 per cent MoS2. From the copper porphyry ores, the recovery of MoS2 is lower, i.e., 30-60 per cent due to the lower MoS2 content in the ore. Figure 1 gives the general flowsheet followed for the extraction of molybdenite from copper porphyry ores. In the first stage, both copper and molybdenum are recovered by flotation with reagents such as xanthate. In the next stage, the xanthate is eliminated by oxidation to render copper nonfloatable, and molybdenum is floated with hydrocarbon addition. Copper is further eliminated from the MoS2 concentrate by leaching with ferric chloride.

Molybdenite Roasting

The MoS2 concentrate is roasted to MoO3 to provide the raw material for molybdenum and ferromolybdenum production. Although the roasting of MoS2 to MoO3 is chemically simple, it requires a good temperature control. This is because at temperatures below 600ºC, the kinetics of roasting is poor and at temperatures above 650ºC the calcine starts to sinter, leading to molybdenum loss due to volatilization of the oxide. The desired temperature control is achieved by employing a Nichols-Herreshoff multiple hearth roaster. The desired sulphur content in the oxide product, i.e., 0.1-0.5 per cent, is achieved in commercial practice by good temperature control.
Molybdenum metal is ultimately produced by the hydrogen reduction of MoO3, in the form of briquettes, at 1000ºC. The metallized briquettes are then pressed into consumable electrodes for melting into molybdenum ingots.

Titanium
Titanium is playing an increasingly important role in this age of special alloys. The strength-to-weight ratio of titanium is very high, almost twice that of steel, and its corrosion resistance is better than even 18-8 stainless steel. Titanium alloys retain their strength even at higher temperatures and show less creep. Minor additions of titanium are sometimes made to enhance the corrosion resistance of stainless steels and reduce thermal stresses by lowering the thermal expansion. One particular alloy used in electrolytic processes has the percentage composition Ti 2.4, Ni 42; Cr 5.4, and Fe remainder. Various Weldable titanium alloys (a typical percentage composition V 13, Cr 11, Al 3, Ti rest) are used in a variety of structural applications for which a combination of properties such as light weight, strength, and corrosion resistance is called for.

Among other applications of titanium, mention may be made of its use as a deoxidizer for ferrous alloys. As a deoxidizer, it is next only to aluminium in strength. Yet, titanium may be preferable to aluminium because the deoxidation product TiO2 has a melting point much lower than that of Al2O3; hence, TiO2 globules float up easily yielding a cleaner steel.

Treatment of Ilmenite for Upgradation
To obtain titanium from ilmenite, the ores must be upgraded to a titania-rich product containing over 90 per cent TiO2. Sometimes, this upgraded ilmenite is known as synthetic rutile. Apart from being the desired raw material for indigenous titanium production, this upgraded concentrate is used for pigment grade TiO2 production and has a good export market.

Ilmenite contains titania and iron oxide in (bound) spinel form and, therefore, cannot be upgraded by physical methods. Most beneficiation methods aim at the removal of the iron oxide by preferential chemical reaction with suitable reagents. The methods used are as follows:
1. The reduction smelting of ilmenite with carbon (and a suitable flux) resulting in a titania-rich slag and pig iron.
2. The direct leaching of ilmenite with acids under atmospheric pressure or high pressure resulting in the preferential dissolution of iron.
3. The selective halogenation of iron oxide to produce volatile iron halides.

Direct Acid Leaching of Ilmenite
As already indicated, the leaching process may have many variations. For example, digestion with concentrated hydrochloric acid is essentially selective whereas that with concentrated sulphuric acid is not. In the latter case, both the oxides are taken into solution. However, subsequent processing of the leach liquor yields titania.

Hydrochloric Acid Digestion of Ilmenite
The hydrochloric acid digestion process has many variations with respect to factors such as temperature, pressure, acid concentration, and prereduction of ferric oxide in the ore. In India, a plant at Tuticorin (Tamil Nadu) has adopted a leaching process for the treatment of about 60,000 tons of ilmenite per year to produce about half as much of synthetic rutile. Here, the ilmenite is prereduced and the reduced iron is leached with dilute HCl, leaving behind high-grade TiO2 as a residue.

Preferential Chlorination of Ilmenite
Iron oxides in ilmenite are easily chlorinated in the presence of carbon by a variety of chlorinating agents. For chlorination, the mineral, taken in a powdery form, is briquetted with charcoal and a binder, for example, asphalt, tar, starch, molasses, or ferric chloride. The use of ferric chloride is said to have several advantages. For instance, it is produced by the chlorination reaction itself. In addition, it has a pronounced
catalytic action on the chlorination of iron oxides. The rate of chlorination of iron oxides depends on several variables. The best results have been obtained by using ferric chloride as a binder, a fine particle size, smaller carbon content in the briquettes, and higher temperature. Better selectivity in chlorination is achieved by using higher temperatures. The chlorinating agents that have been used are chlorine, hydrogen chloride and various gas mixtures such as chlorine-hydrogen chloride, and carbon monoxide-chlorine.

The chlorination of ilmenite at 500-600°C in the presence of carbon (as about 6 per cent charcoal) and a FeCl₃ binder yields a product that contains about 90 per cent TiO₂. The reaction may be accelerated by catalysts such as CuO, PbO, MnO₂, CaO, CeO, and Ca₃(PO₄)₂. By increasing the temperature to 900-1000°C, we can obtain a residue richer in TiO₂ (95-98 per cent).

As already indicated earlier, TiO₂ itself is subsequently chlorinated to give crude TiCl₄. This crude TiCl₄ is purified by several techniques. For instance, dissolved-gases may be removed by using inert gases and more volatile impurities such as SiCl₄ are removed by fractional distillation.

Production of Metallic Titanium by Reduction of Titanium Tetrachloride

Thermodynamic calculations indicate that TiO₂ can be reduced either by carbon or other metals. Carbon reduction, however, is likely to produce the brittle carbide and magnesium reduction leads to a product that is contaminated with TiN and TiHₓ. The alkali reduction of TiO₂ is possible only at very high temperatures. Consequently, the halide route has always been more attractive for the production of titanium. The oxide TiO₂ can be easily chlorinated by chlorine at about 600°C in the presence of carbon. The resulting chloride, namely, TiCl₄, serves as the main raw material for all reduction reactions. It may be noted that the efforts to produce the metal through the electrolytic reduction of TiO₂ have largely been unsuccessful.

The magnesium reduction of TiCl₄ has been extensively studied at BARC, Bombay. The chlorination TiO₂ has been carried out using a temperature of 820-860°C in an argon atmosphere, the reduction time being 5 hours. A maximum yield of about 85 per cent has been obtained using about 40 per cent excess magnesium. Any additional amount of magnesium is not beneficial. The average iron content at 860°C, due to the iron pick-up from the reaction chamber, is about 0.2 per cent. Bimetal reduction-using a mixture of magnesium and about 15 per cent sodium as the reducing agent-is said to markedly improve the yield of titanium sponge to about 96 per cent. Also, the sponge has a relatively lower iron content. As already mentioned, similar advantages have been noted also in the case of reduction of ZrCl₄ by Mg-Na mixtures. The introduction of sodium into the system is said to bring about the following effects:

(1) NaCl, which is formed as a result of the reaction of sodium, acts as an efficient scavenger with respect to impurity chlorides such as FeCl₃ and AlCl₃.
(2) NaCl, because of its better heat conductivity than MgCl₂, prevents, to a large extent, local overheating at isolated spots during the exothermic reduction reaction.
(3) NaCl-MgCl₂ compositions are more fluid, leading to a better separation of metal from slag, a purer metal after distillation, and excess metal.

Production of Ductile Titanium

As stated in Section 8.20, the brittle sponge produced by Kroll's process can be converted to ductile titanium by various processes. Firstly, the sponge is purified. Vacuum distillation at pressures less than 100 microns and at temperatures of about 900°C for a period of 30-40 hours effectively removes the small amounts of residual MgCl₂ and magnesium. The products are cooled in an argon atmosphere and then dry air is flushed to remove the traces of volatile chlorides. This complicated purification procedure nearly doubles the price of the metal.

Next, the sponge is melted. For melting, a carbon crucible is used which leads to about 0.5 per cent carbon contamination in the metal. The metal also contains small amounts of Mg, Fe, and Si. Melting must be done in oxygen-free atmosphere.
The metal sponge can also be purified by the iodide process. However, this process has not found wide commercial application because of an extremely low rate of production. Better success has been obtained using powder metallurgy techniques for consolidating and briquetting the sponge.

It has been shown that the mechanism of the reaction of sodium with titanium subchlorides in fused sodium chloride is of an electrochemical nature. The model is the same as that proposed for the galvanic corrosion of iron in an acidic solution containing oxygen (see Fig. 3).

A great deal of evidence has been put forward to support the aforementioned postulates. The most interesting observations are as follows. Titanium always grows from metallic surfaces and the reaction is inhibited if the reactor wall is made of a material which does not conduct electricity, e.g., a ceramic coating on a steel reactor. In reactions, where complete reduction is forced to take place in the gas phase (a molecular rather than an electrochemical reaction), the titanium produced is obtained in a pyrophoric powder form rather than as crystals. An ionic reaction deposits the metal ion on an existing particle of titanium. Then the ion discharges itself and positions itself favourably with respect to the substrate, the continuing phenomenon giving a crystalline material. In a molecular reaction; individual particles of the metal seldom come together to form coherent masses of bigger particles.