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Bureau of Mines Development of Titanium Production Technology

By J. L. Henry, W. W. Stephens, D. D. Blue, and J. H. Maysilles

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UNITED STATES DEPARTMENT OF THE INTERIOR
Donald Paul Hodel, Secretary

BUREAU OF MINES
David S. Brown, Acting Director

As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural resources. This includes fostering the wisest use of our land and water resources, protecting our fish and wildlife, preserving the environment and cultural values of our national parks and historical places, and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to assure that their development is in the best interests of all our people. The Department also has a major responsibility for American Indian reservation communities and for people who live in island territories under U.S. administration.

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PREFACE

The use of titanium metal and its alloys in the United States has been increasingly important to the Nation's economic structure and strategic capabilities since it became commercially available in 1948. Its high strength-to-weight ratio and integrity in corrosive environments have made titanium the preferred material of construction for many applications. The major demand to date has been for turbine engine parts and airframes, and its use is now standard practice in these and other key areas.

Two important developments in titanium use and production have recently emerged. First, the use of titanium for industrial applications is increasing steadily and significantly. Its ability to resist corrosion in many environments has led to uses in critical industries such as electric power production and chemical processing. It has become competitive with alloys that contain materials such as chromium, cobalt, and nickel, which are in short domestic supply for applications in key areas. Titanium sources are plentiful in the United States, and the ability to use domestically available materials in place of imported substances is an important factor in reducing the Nation's mineral supply vulnerability.

A second development is the increased interest in finding alternative methods for recovering the raw metal from resource materials. Price of the final product has always been a major barrier to more extensive use of titanium, and cost reductions in all phases of production have been sought continually. Most processing investigations reported to date have been concerned with refinement of the base metal and fabrication methods. As recently as 1980, in symposia proceedings and other published collections of papers, very few presentations dealt with the recovery and production of the base metal; most discussed properties and applications of alloys and fabrication technology. In the last few years, however, interest in extraction and recovery cost reductions has been more active, even though few investigations are being reported.

In view of these developments, this publication reviews the status of titanium extraction technology and identifies approaches that could lead to significant advances in this area. Research accomplishments of the Bureau of Mines, U.S. Department of the Interior, are highlighted in this review because the Bureau has been instrumental in developing the processes that are presently used by industry. The Bureau has also made pioneering studies of alternative recovery techniques, and some of these investigations have recently been continued by the private sector. These techniques may form the basis for important developments in titanium production that lead to greatly expanded availability of this strategically important material.

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

A	ampere
A·h	ampere hour
A/cm^2	ampere per square centimeter
A/dm^2	ampere per square decimeter
A/ft^2	ampere per square foot
A/lb	ampere per pound
Å	angstrom
Å/mm	angstrom per millimeter
atm	atmosphere, standard
Be	Baume
Btu	British thermal unit
Btu/lb	British thermal unit per pound
(Btu/lb)/°F	British thermal unit per pound per degree Fahrenheit
cm	centimeter
cm^3/(min·cm^2)	cubic centimeter per minute per square centimeter
cm^3/min	cubic centimeter per minute
cP	centipoise
°C	degree Celsius
°F	degree Fahrenheit
F	farad
F/mol	farad per mole
ft	foot
ft^2	square foot
ft^3	cubic foot
ft^3/min	cubic foot per minute
g	gram
ga	gauge
gal	gallon
gal/h	gallon per hour
g/L	gram per liter
g/min	gram per minute
g/cm^3	gram per cubic centimeter
h	hour
HB	Brinell hardness number
hp	horsepower
in	inch
in Hg	inch of mercury (atmospheric pressure)
K	kelvin
kg/d	kilogram per day
kg/h	kilogram per hour
kV·A	kilovolt ampere
kW	kilowatt
kW·h	kilowatt hour
kW·h/lb	kilowatt hour per pound
kW·h/st	kilowatt hour per short ton
lb	pound
lb/d	pound per day
lb/h	pound per hour
lb/ft^3	pound per cubic foot
lbf	pound (force)
lbf/in^2	pound (force) per square inch
lbf/in^2(ga)	pound (force) per square inch, gauge
lb/gal	pound per gallon
L/min	liter per minute
mA	milliampere
μm	micrometer
μm Hg	micrometer of mercury
min	minute
Mkg/yr	million kilograms per year
mL	milliliter
mL/min	milliliter per minute
mm Hg	millimeter of mercury
MMlb/yr	million pounds per year
mt/d	metric ton per day
nm	nanometer
oz	ounce
pct	percent
ppm	part per million
r/min	revolution per minute
s	second
st	short ton
st/d	short ton per day
st/yr	short ton per year
V	volt
vol pct	volume percent
W	watt
wt pct	weight percent
yr	year

BUREAU OF MINES DEVELOPMENT OF TITANIUM PRODUCTION TECHNOLOGY

By J.L. Henry,[1] W.W. Stephens,[2] D.D. Blue,[3] and J.H. Maysilles[4]

ABSTRACT

The development and status of technology for producing titanium from U.S. resource materials are summarized in this Bureau of Mines report. Commercially feasible processes and investigations of alternative procedures are reviewed in order to identify techniques that could make existing operations more effective or areas in which future research may lead to the development of new production methods. Procedures are described for producing concentrated titanium dioxide from starting materials such as sands, massive deposits, and mineral processing residues containing rutile, ilmenite, and perovskite; producing and purifying titanium tetrachloride from concentrated rutile, ilmenite, and titaniferous slags; reduction of titanium tetrachloride to titanium sponge metal using metallic magnesium or sodium; purifying and consolidating titanium sponge and scrap by arc melting or induction melting techniques; purifying sponge, scrap, and alloys by molten salt electrorefining; and electrowinning titanium from chloride salts.

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INTRODUCTION

The two most important titanium-containing products manufactured in the United States, by volume and dollar value, are titanium metal and titanium dioxide pigment. In 1985, 23,000 st of raw metal valued at $173 million was produced and 860,000 st of pigment valued at $1,307 million was produced. These two products accounted for more than 96 pct of domestic titanium production. Of all titanium products, the metal is of particular interest because of its economically and strategically important applications.

Although the existence of titanium was first reported in 1791, the properties of the metal were not known until the 20th century. High-purity titanium was first prepared in 1910, and an extensive series of investigations to determine its physical and mechanical properties was made between 1925 and 1940. The suitability of titanium and its alloys as construction materials gradually became apparent.

The density of titanium is less than 60 pct that of steel. High-purity titanium has insufficient mechanical strength to be a significant structural material, but its plastic properties are substantially changed by small amounts of impurities. Interstitially soluble elements, which include oxygen, nitrogen, carbon, and hydrogen, have very great strengthening and embrittling effects at ambient temperature. Titanium also forms extremely hard metallic compounds with carbon, nitrogen, boron, and silicon, which are very resistant to abrasion.

Titanium can retain useful structural properties from -180° to over 500° C, depending on the particular alloy and application. Within this range, hydrogen can be absorbed above 150° C, and oxygen and nitrogen are absorbed above 700° C, with embrittlement and loss of ductility resulting. Fortunately, many forming operations can be carried out at ambient temperatures. Titanium must be protected from air during melting operations, however.

Titanium alloys resist fatigue damage. They are also tough; high loads are required to cause failure in the presence of defects or cracks. These factors allow a long service life. Thus, the combination of high strength, low density, good fatigue and abrasion resistance, and toughness allows design of highly efficient structures.

The largest market for titanium to date has been for military and civilian aircraft. It is used mostly in turbine engine parts that are operated within the temperature limits of the alloys. It is also used in airframe parts, particularly those subjected to relatively high temperatures.

Although new alloys and fabrication techniques are still being developed, the use of titanium in the aerospace industries appears to have reached a high level of maturity. In recent years, the area in which use has increased most steadily is the industrial sector. The corrosion resistance of titanium under a variety of conditions has made it a cost-effective material for many types of equipment. In 1983, 60 pct of U.S. titanium metal consumption was for use in aerospace applications; 20 pct for other industrial uses such as the chemical industry, power generation, and marine and ordnance applications; and 20 pct in steel and other industries.

Titanium exhibits excellent corrosion resistance to seawater, chloride solutions, organic media, petrochemical products, and several acids, especially under oxidizing conditions. Alloy additives significantly increase resistance to reducing media and can possibly extend the useful temperature range beyond the normal service limit of 250° C. Also, alloy welds exhibit corrosion resistance equal to that of the base metal.

The major industrial use of titanium is in heat-exchange equipment, such as salt-water-cooled power-plant condensers. Although initial cost is high, it is a cost-effective material because downtime is eliminated or greatly reduced. Heat transfer is improved by eliminating corrosion scale and fouling, and reliability needed for nonpolluting operations is provided. In many such applications titanium is replacing widely used stainless steels and nickel-base alloys.

Titanium has important applications in many industries. In chemical processing industries it is used to make dimensionally stable electrodes for electrochemical processes to win copper and zinc from acid solutions, for example. Titanium also has wide applicability in food and drug processing and biomedical use because of its chemical inertness and low toxicity. In energy industries, potential uses include steam turbine blades, pipe for deep gas wells, and geothermal processing equipment.

Titanium is presently used throughout the world in heat exchangers, chemical reactors, piping, pumps, and similar equipment. Its reliability in service is now demonstrated, and its limitations are better defined. Many early problems have been identified and overcome. New applications are continuously being sought and found. Its use in many key applications now depends to a great extent on its availability and price.

BACKGROUND

The Bureau of Mines has assumed major responsibilities for minerals exploration, including the assessment of titanium source materials and the development of technologies for recovering titanium metal. Efficient use of natural resources is a high national priority, and the Bureau has a primary responsibility for investigating methods to responsibly develop the Nation's mineral resources. Related issues, such as national defense capabilities, efficient use of energy resources, environmentally sound activities, and invulnerability to materials supply disruption have been brought into national focus.

Evaluation of domestic ore deposits for mineral recovery potential has been an important continuing Bureau program. Investigations of titanium source materials began in 1913 with an assessment of titaniferous iron ores (*188*).[5] The goal of the study was the recovery of iron, but in the reported experimental work a titanium-

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[5] Italic numbers in parentheses refer to items in the list of references at the end of this report.

rich byproduct was produced as a slag when the ore was smelted. The smelting technique became the basis for subsequent investigations to recover titanium as well as iron.

A more extensive program of mineral deposit exploration was initiated in response to passage of the Strategic and Critical Materials Stock Piling Act. The primary goal of this exploration program was to effectively utilize mineral resources to make the greatest possible contribution to national security and economy. A great number and variety of deposits containing titanium and important associated minerals have been evaluated as part of this continuing program in cooperation with property owners, industry, State and local governments, universities, and other Federal Government organizations (*20, 22-23, 29, 42-43. 54-55, 58-59, 66, 75-78, 90-91, 94, 102-103, 118; 128, 165, 173-174, 180, 188-189, 193, 196-198, 203-204*).

By 1922, the Bureau had received numerous inquiries about titanium, and a publication describing properties and uses of titanium metal and compounds to the extent they were known was issued in response (*4*). In later years, potential uses for the metal became better defined, and in 1938 a research program was begun by the Bureau to survey titanium preparation methods that might be adapted to commercial-scale production. In 1941, a reactor was built in which titanium sponge metal was produced in batches of a few grams by reducing titanium tetrachloride with magnesium metal, as described and patented by W. J. Kroll (*113*). In 1944, a program of regular production was begun, and by 1948, batches of over 100 lb were being produced on a regular basis (*61*). Commercial production began that year, and the Kroll magnesium reduction process as developed to production scale by the Bureau of Mines has been commonly used by the industry to this day.

Interest in developing strategic applications of titanium began during the Bureau's first production program. Authorized and financed under cooperative agreements with the Defense Materials Procurement Agency and the Army Ordnance Corps, the Bureau operated a pilot plant from 1952 to 1954 to improve reduction process techniques and produce high-quality sponge metal. Many subsequent product consolidation, fabrication, and application studies have been made under sponsorship of the Departments of the Army, Navy, and Air Force, including melting and casting, arc welding, metal and alloy plate production, and properties of alloys.

As the development of large-scale titanium production proceeded, the need for good process control to ensure product quality became apparent. Under an agreement with the General Services Administration, the Bureau evaluated and developed analytical techniques to measure impurity element concentrations in titanium tetrachloride, magnesium metal, intermediate products, and titanium sponge as a means to maintain high product purity.

Corrosion-resistance properties of titanium were first investigated by the Bureau of Mines in the 1940's, and by the early 1950's a well-established research program was in effect. Early studies showed that corrosion-resistance properties of titanium exceeded those of some stainless steels, and potential for its use in chemical industries and marine environments became evident.

The greatest advance in industrial use of titanium began in 1968 as part of the Nation's effort to meet its energy needs by developing new energy sources and more energy-efficient systems. Suitability of titanium for use in acid mine water environments had already been investigated by the Bureau in the 1950's (*5*), and an extensive program to evaluate applications of titanium and other metals and alloys for use in geothermal energy systems has been carried out since the 1970's, under an agreement with the Department of Energy.

Other applications related to energy recovery have derived from other useful properties of titanium and its compounds. Supported in part by the Department of Energy, the Bureau investigated methods for coating critical surfaces of valves and other devices in coal gasification units with abrasion-resistant materials. The use of materials, such as titanium diboride, that are nonsparking and also hard and wear-resistant in fabrication or coating of cutting tools for coal mines and other potentially explosive environments also has been studied.

Resource conservation and environmental issues have been addressed by Bureau research for titanium recovery. In 1950, methods to recover ilmenite and iron oxide from aluminum recovery process wastes were reported. Since passage of the Solid Waste Disposal Act in 1965, the Bureau has increased research efforts to recover valuable constituents from industrial and domestic wastes. Recovery of titanium and other metals from titanium chlorination plant wastes and alumina plant residues has been investigated, and waste recycling in titanium plant operations has been studied.

Another important national issue is the availability of materials that are strategically important and critical to the Nation's economy. Titanium sponge metal and rutile, the most commonly used titanium dioxide mineral, are considered strategic and critical materials. Titanium is a key commodity in this issue for two reasons.

First, although domestic source materials are plentiful, much titanium raw material is now imported, particularly rutile, which is the preferred starting material for metal production. Economical methods for recovering titanium from low-grade domestic sources are now being sought with great interest. The Bureau has been making investigations in this area for many years. In the 1950's, research was started on a smelting process to produce pig iron and titaniferous slag from ilmenite and other titaniferous iron minerals. Many smelting techniques and methods for recovering titanium from slags have been studied, partly under sponsorship by the Department of the Army and by the General Services Administration.

Efforts to expand domestic rutile production have also been made. In 1967, the Office of Emergency Planning established a production goal of 70,000 st/yr. The Bureau of Mines has since investigated the feasibility of both rutile recovery from a number of source materials and production of synthetic rutile from other titanium minerals.

A second reason for the importance of titanium in the minerals availability issue is its potential to replace imported and domestically scarce materials such as chromium, cobalt, and nickel in many applications.

The current status of titanium demand, potential applications, and production capabilities indicates a strong interest in developing more effective and economical technology for recovering the raw metal from low-grade domestic sources. Titanium recovery from source materials has been a subject of extensive investigations by the Bureau of Mines, and it seems likely that important future developments will be derived from those investigations.

ACKNOWLEDGMENTS

The research performed in the Bureau of Mines facilities at Tucson, AZ; Salt Lake City, UT; and Boulder City, NV, reported in this Bulletin was compiled by the authors from laboratory notebooks, unpublished progress reports and monographs, and Bureau Reports of Investigations and articles in the technical press. The research represents the efforts of scores of workers, and no attempt will be made to acknowledge all of the contributors. The source materials, and thus the major workers, are noted at the heading of sections by references to published reports.

Substantial financial support for the pilot-plant developments and for construction and initial operation of the magnesium reduction demonstration plant was provided by the Ordnance Corps, Department of the Army. The research on development of continuous reactors, including the initial work on sodium reduction of titanium tetrachloride was also funded by the Ordnance Corps.

Continuous operation of the demonstration plant was conducted under a contract with the Defense Materials Procurement Agency that called for production of 500,000 lb of titanium over a 15-month period.

The Wah Chang Corp., New York, provided funds and technical support for experimental intermittent operation of the development plant over a 15-month period. In addition to the financial assistance, the technical contributions, supervision, and leadership of Dr. Steve Yih and Dr. C. L. Lo of the Wah Chang Corp. were of value in determining factors that affected the hardness of titanium sponge produced by the reduction of purified $TiCl_4$ with magnesium metal.

CHAPTER 1.—TITANIUM SOURCE MATERIALS

In 1983, U.S. reserves in both rock and sand deposits were estimated to contain 10 million st of titanium in ilmenite and 1 million st in rutile, with a total reserve base of 33 million st of contained titanium (*125*). The reserve base is the in-place demonstrated resource from which reserves are estimated and includes those resources that are currently economic, marginally economic, and some that are currently subeconomic. Reserves are that part of the reserve base that could be economically extracted or produced at the time of determination and include only recoverable materials. The United States has ample supplies of titanium to meet its foreseeable future needs, provided that recovery technology exists (*126*).

Titanium source materials are also important for reasons other than their recoverable titanium. Titaniferous materials usually contain important associated mineral values. Most titaniferous deposits contain large amounts of iron. The United States presently imports nearly one-fourth of its iron ore for consumption, and development of these domestic materials would reduce this import need. Zirconium and hafnium, which have applications in nuclear power generation, are recovered from zircon sand, and are produced as byproducts of ilmenite and rutile production. Other materials associated with titanium sources include chromium, columbium, tantalum, thorium, uranium, vanadium, yttrium, rare-earth elements, and alumina.

Significant amounts of titanium also exist in waste products from mineral recovery operations. Recovery of titanium and other values from these materials would increase domestic production of these values and could result in reduction of hazards associated with the wastes and improved economy of existing operations.

Titanium is presently recovered from two minerals: rutile and ilmenite. Rutile is the most common naturally occuring form of titanium dioxide (TiO_2). Other forms include brookite and anatase (also known as octahedrite). These minerals are also natural forms of TiO_2. Commercial rutile concentrates contain about 95 pct TiO_2. Rutile is the preferred raw material for metal production, but a relatively small fraction of titanium occurs as this mineral. The U.S. rutile reserve base in 1985 was about 1 million st of titanium content; economic deposits contained approximately 200,000 st and marginally economic and some currently subeconomic deposits contained about 700,000 st.

Ilmenite ($FeO{\cdot}TiO_2$ or $FeTiO_3$) is the more common titanium resource mineral. U.S. ilmenite reserves were estimated to contain 7.9 million st Ti in 1985. The concentration of titanium in ilmenite and related minerals varies considerably. Pure ilmenite contains 53 pct TiO_2, but in some sand deposits natural beneficiation has occurred. Some iron has been oxidized and then leached to form an alteration product known as leucoxene, which is essentially pure TiO_2. Concentrations of TiO_2 in these materials run as high as 70 pct. In contrast, much titanium occurs in lower grade materials. Ilmenite is often associated with iron minerals such as magnetite, and TiO_2 concentrations in large deposits are commonly less than 20 pct.

Titanium production has historically come from two types of deposits: beach sands and stream placers and massive deposits of titaniferous iron ores that occur in igneous complexes in which ilmenite is associated with anorthosite and gabbro. Rutile and ilmenite often occur together in sands, and most ilmenite and all current U.S. rutile reserves exist in this type of deposit in Florida, Georgia, New Jersey, and Tennessee. Beach and dune sands have been extensively evaluated since the 1940's as sources of titanium and other mineral values, and the Bureau developed heavy-liquid techniques for field use in determining the heavy-mineral content of sands (*29*). These techniques were used to help evaluate deposits containing rutile, ilmenite, and other minerals such as zircon and monazite, which contains thorium and rare-earth elements

Hard-rock deposits of titaniferous iron ore in New York account for about 30 pct of U.S. ilmenite reserves. No current rutile reserves are in massive deposits, but one such potential resource exists in Arkansas. Titanium content of the various deposits averages 2.5 to 3 pct, mostly as rutile but with other minerals present, all intimately associated with the gangue material. The Arkansas property was operated briefly in the 1940's. Complexity of the mineralization may be a difficult problem to overcome in future recovery schemes. Other significant titanium source materials exist but are not presently being developed. Two relatively common titanium minerals not being processed are perovskite and sphene. Identified perovskite ($CaO{\cdot}TiO_2$ or $CaTiO_3$) deposits in the reserve base contain 6.5 million st TiO_2. Recovery awaits development of an economical process, and the Bureau is currently making investigations in this area. Sphene ($CaO{\cdot}TiO_2{\cdot}SiO_2$ or $CaTiSiO_5$) may never become a source of titanium, as recovery promises to be more difficult than from competitive materials such as ilmenite.

Potentially recoverable titanium has been identified in mineral processing waste products. Byproducts of sand and gravel operations and placer gold mining contain rutile, ilmenite, and other minerals. Copper mill tailings and titanium chlorination process residues contain rutile. Residues from the Bayer process for recovering alumina from bauxite contain titanium essentially as ilmenite. A number of byproduct sources thus exist from which titanium might be recovered by methods similar to those now being used or developed for primary source materials.

PHYSICAL BENEFICIATION OF SOURCE MATERIALS

In many source materials, titanium minerals are separable from associated minerals by physical methods. Differences in physical properties such as particle size and shape, density, magnetic permeability, dielectric constant, and surface characteristics allow separation of rutile and ilmenite from other valuable minerals and from gangue materials.

Physical separation techniques, when applicable, can be used to economically concentrate minerals while producing a minimum of waste for disposal or byproducts. The use of physical beneficiation has been economically essential to all commercial titanium recovery operations used in this country (*54, 64, 165, 190, 201, 211*). Florida sand contains less than 5 pct heavy minerals. Using the methods outlined in figure 1, for example, approximately

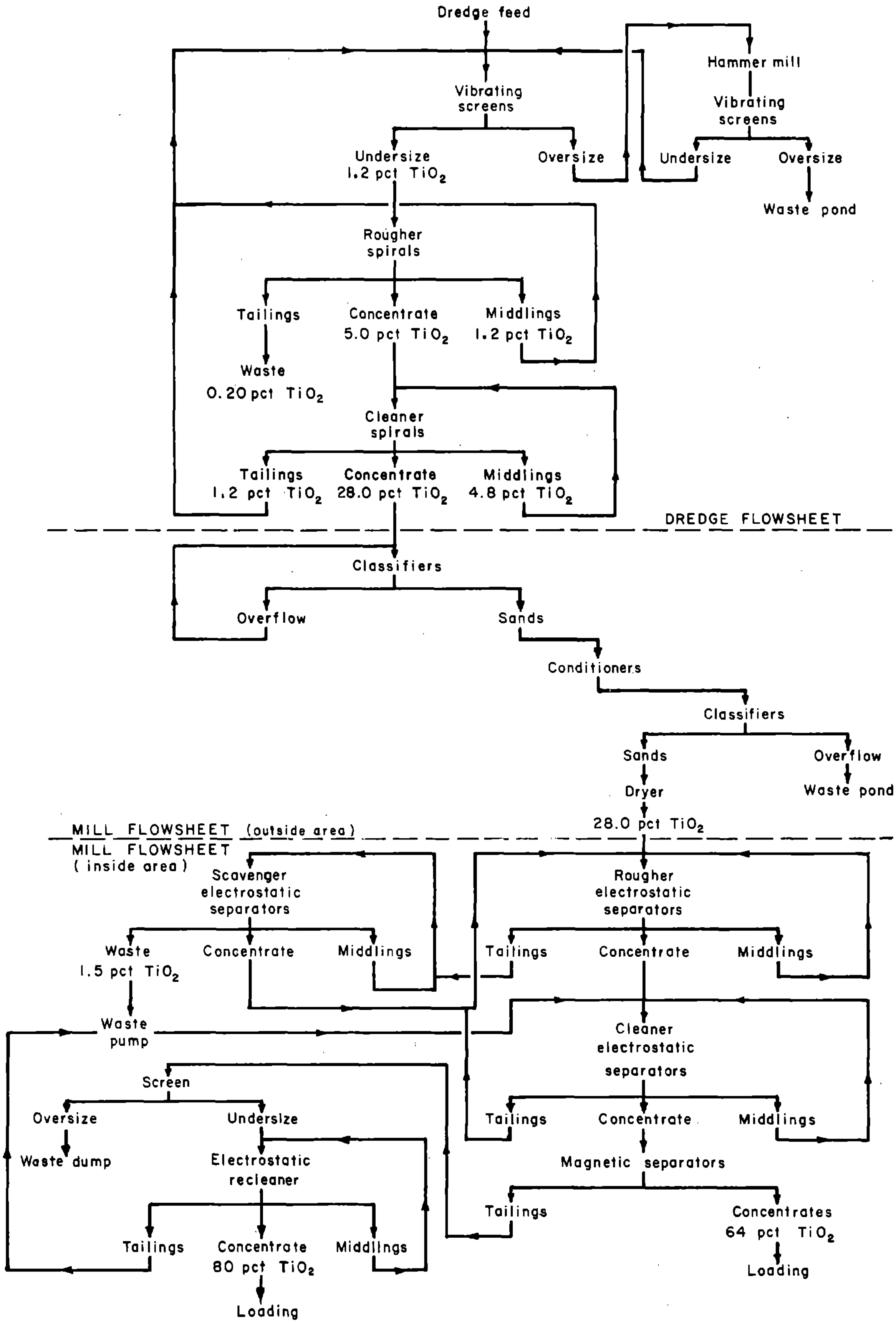

Figure 1.—Flowsheet for Highland plant of E.I. du Pont de Nemours & Co.

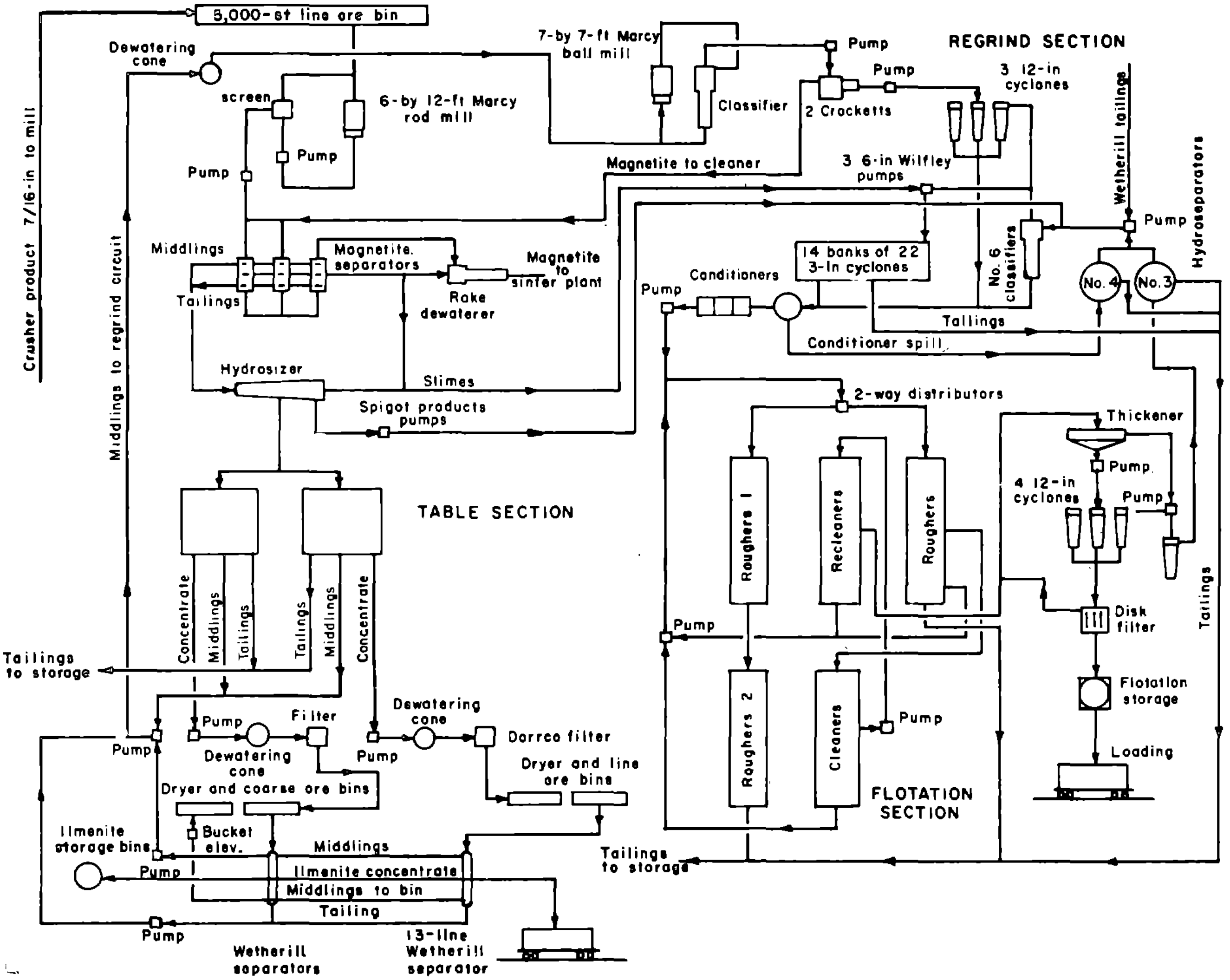

Figure 2.—Flowsheet for Tahawus, NY, plant of National Lead Co.

80 pct of the titanium has been recovered from feed that contains less than 2 pct titaniferous material (*64*, *165*). The product is a mixture of ilmenite, leucoxene, and rutile. From a massive New York hard-rock deposit averaging 32 pct ilmenite and 37 pct magnetite, methods outlined in figure 2 have been used to produce a concentrate containing 45 to 47 pct TiO_2 (*126*, *165*). The Bureau has investigated a number of titanium-containing materials for amenability to concentrating the titanium minerals by physical methods.

Sand Deposits

Many titanium source materials are in the form of sands or unconsolidated materials in which the component minerals exist to a large degree as discrete particles. Expensive grinding operations necessary for liberating the minerals in these materials are therefore minimized.

Several beach and placer sand deposits have been evaluated as titanium resources (*180*, *202*, *204*). These materials are already beneficiated to an extent by natural causes. Action of the water in ocean waves and in streams has produced concentrations of heavy minerals and washed away most particles that are too fine to respond well to physical beneficiation methods. The most common titanium mineral is ilmenite, but some rutile, leucoxene, and sphene are also found. The deposits examined generally contained 1 to 9 pct TiO_2 and up to 42 pct Fe, with other values such as zircon and monazite present in some deposits. The heavy minerals were generally recoverable in a bulk concentrate using standard hydraulic classification equipment such as Humphreys spirals and tables, but the recoverability of separate titanium minerals varied considerably. In one sample, 82 pct of the ilmenite was recovered in a 44-pct-TiO_2 concentrate by screening, separation of screen fractions, oxidizing and reducing roasting, and electrostatic and magnetic separation methods (*76*). In other samples, titanium was not effectively separated even when careful stage grinding was used, particularly for materials in which the minerals were not liberated at sizes greater than 200 mesh.

Other deposits examined were mixtures of sands, clays, silts, and sandstones (*75*, *77-78*, *206*). In clays, a large fraction of titanium was locked in particles too small to be concentrated. Sandy materials gave various responses as described previously. Some concentrates contained chromium, columbium, manganese, and vanadium.

Mineral Processing Residues

Many residues from existing mineral processing operations consist of material already reduced sufficiently in particle size to liberate titanium minerals and are beneficiated to some extent by removal of the primary values. Some residues are from titanium extractive metallurgy processes and contain unreacted TiO_2.

The Bureau has examined byproducts from many sand and gravel and placer gold recovery operations in the southeastern United States and in California (*39, 67-68*). Heavy minerals could be concentrated by wet-gravity methods. Ilmenite, rutile, zircon, monazite, magnetite, gold, platinum-group metals, thoria, and chromite could be separated to some extent from various materials tested. Figures 3 through 5 outline recovery methods developed for some of these byproducts.

Residues from some bauxite recovery processes contain significant amounts of titanium and other valuable minerals (*26, 33, 63, 148, 206*). Black sand from an Arkansas operation contains 4 pct TiO_2, 30 pct Fe, and about 0.07 pct Cb. Gravity concentration and desliming recovered 71 pct of the TiO_2 and 65 pct of the Cb in a concentrate containing 9.6 pct TiO_2, 0.17 pct Cb, and 41 pct Fe. Roasting and magnetic separation of the concentrate gave a magnetic product containing 89 pct Fe in the concentrate and a nonmagnetic product containing 91 pct TiO_2 and 95 pct Cb. A proposed flowsheet for concentrating ilmenite and iron minerals is given in figure 6.

A red mud residue from the same process contained 3.9 pct TiO_2 and 0.16 pct Cb. This material was 82 pct minus 325 mesh. Physical beneficiation methods used were ineffective, and the use of a centrifuge was suggested if further concentration tests were to be made.

Titanium chlorination plant wastes are another promising source for titanium (*134-135, 155*). Samples examined in the latest tests contained 19 to 55 pct TiO_2. Although the materials were more than 50 pct minus 200 mesh, screening and wet-gravity techniques were developed that produced concentrates containing 69 to 91 pct TiO_2 with recoveries of 69 to 89 pct, after soluble materials had been leached away. Unreacted coke from the chlorination reaction was removed by selective carbon flotation. The recovery scheme is shown in figure 7.

Tailings from some copper milling operations contain rutile. One porphyry ore tailing sample contained about 0.75 pct TiO_2, about 0.50 pct as rutile. About half the rutile was considered recoverable. In the plus 200-mesh particles, 80 pct of the rutile was locked, whereas in the minus 200-mesh sizes, more than 70 pct was liberated. Small particle size limited the effectiveness of conventional gravity and magnetic separation methods. The material was sized, ground, and deslimed. Flotation techniques recovered 76 pct of the recoverable TiO_2 in a 43-pct-TiO_2 concentrate.

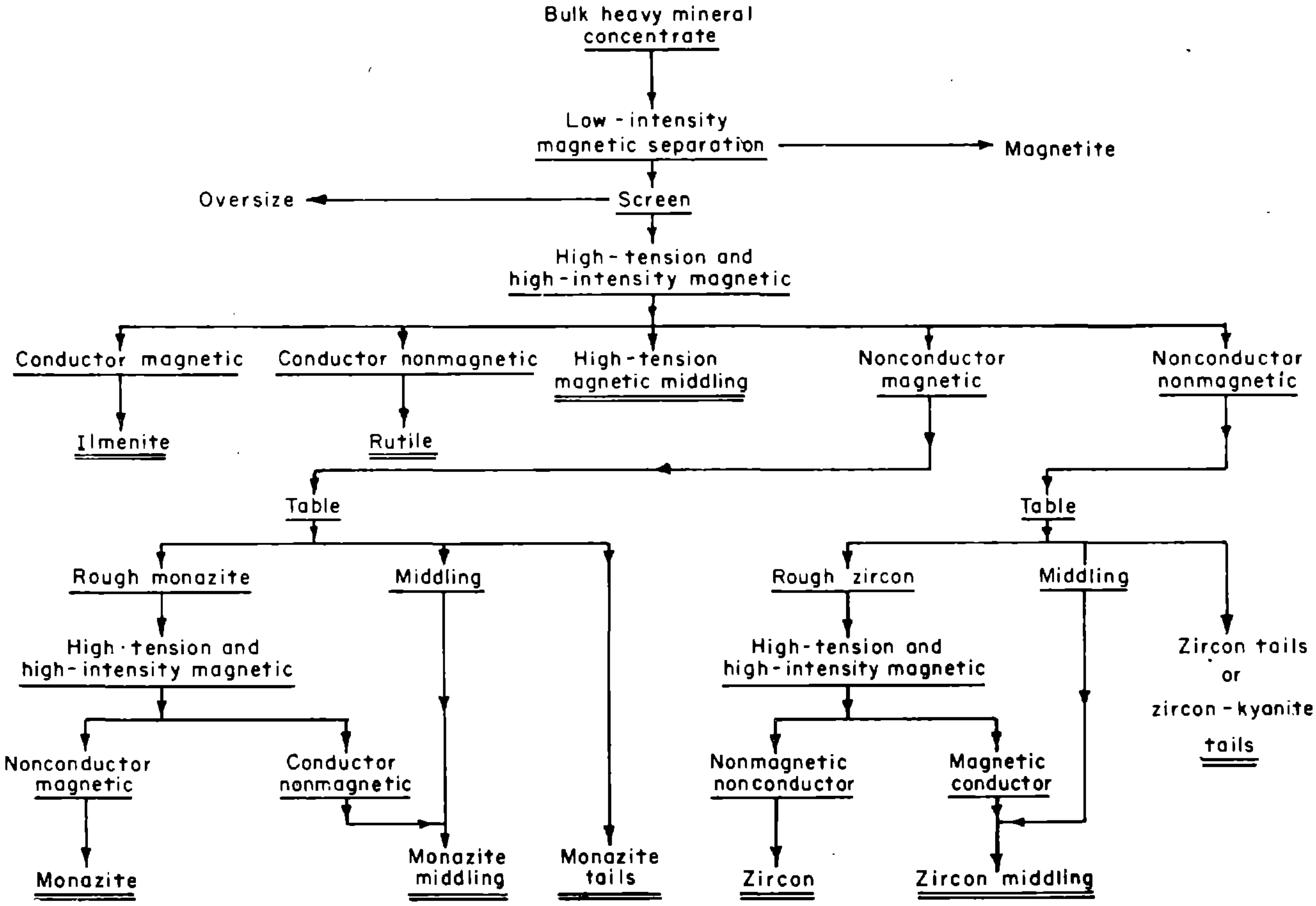

Figure 3.—General flowsheet for fractionation of heavy mineral concentrate.

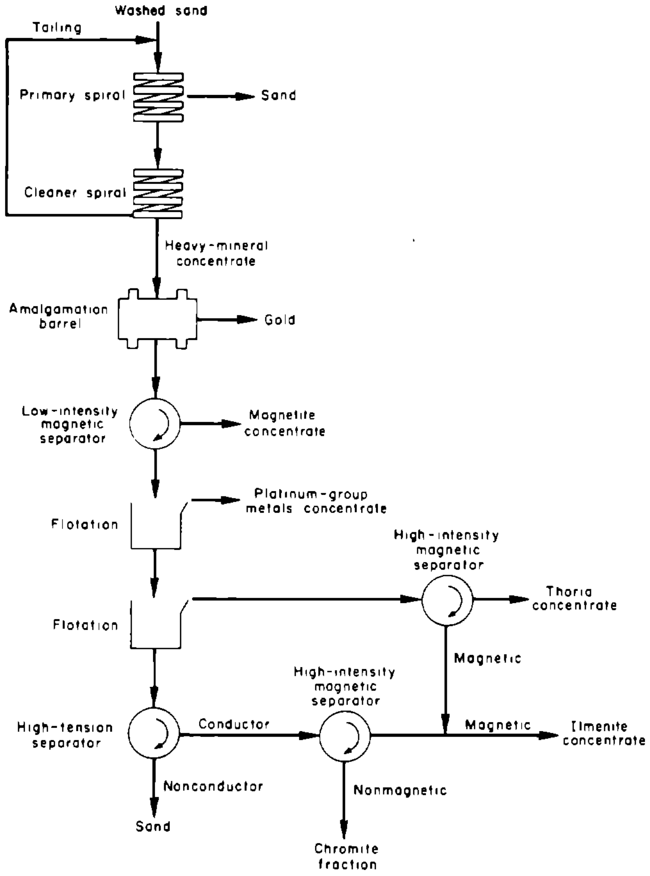

Figure 4.—Processing sequence for Merced and San Joaquin Rivers sand.

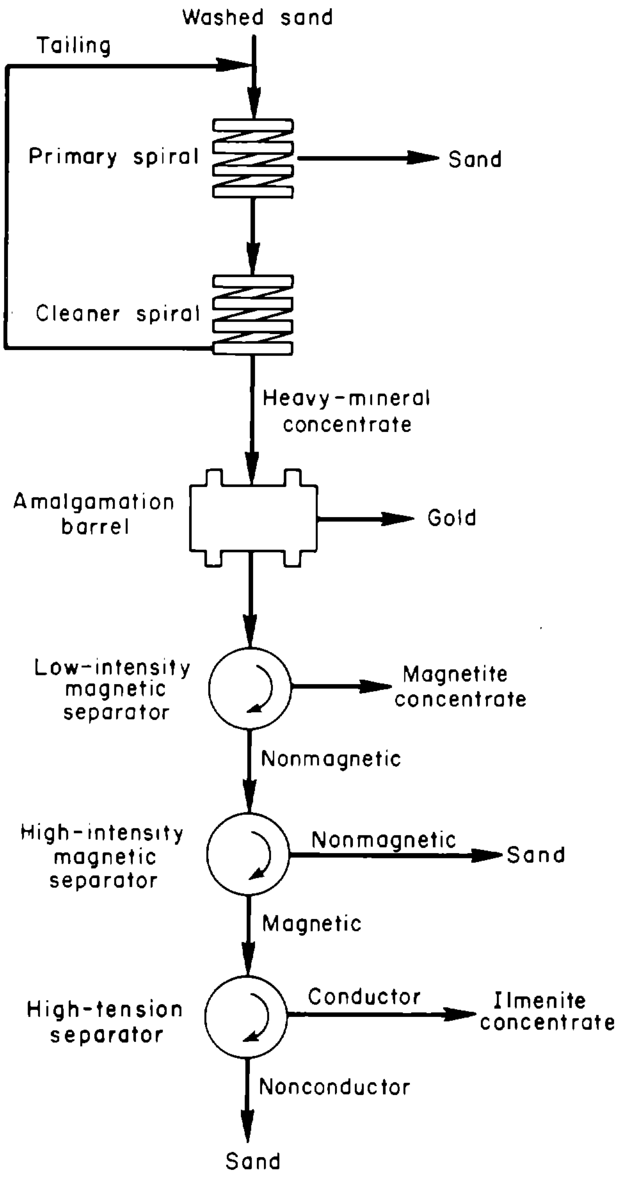

Figure 5.—Processing sequence for Big Tujunga, San Gabriel, Otay, and Sweetwater Rivers sand samples.

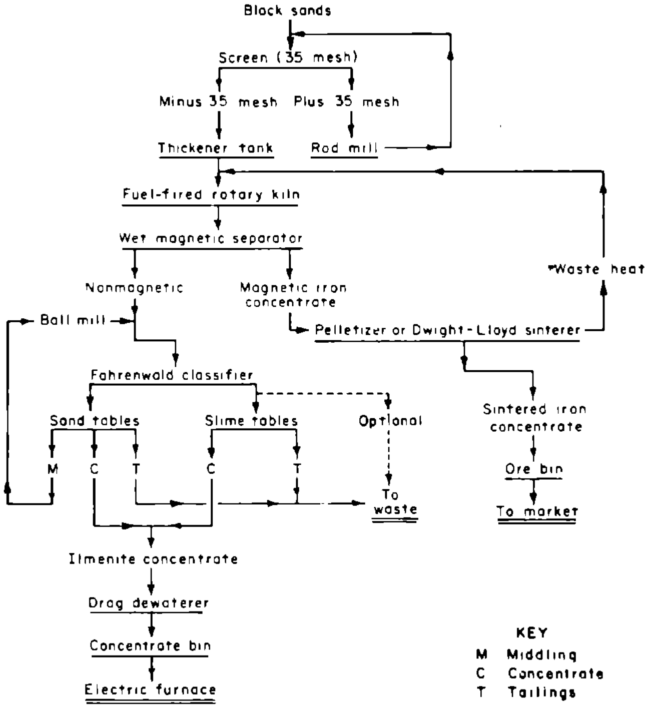

Figure 6.—Proposed general flowsheet for milling black sands.

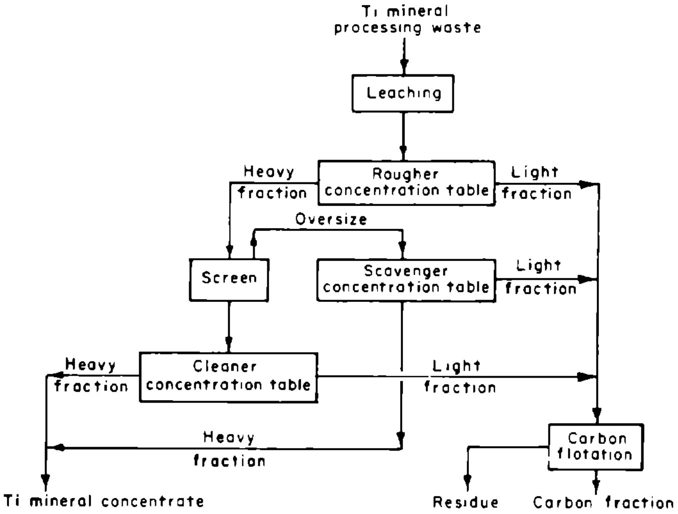

Figure 7.—Gravity concentration scheme.

Massive Deposits Containing Titanium Dioxide Minerals

Only a few massive hard-rock deposits have been assessed for recovery of TiO_2 minerals. Most investigations made have been on two Arkansas deposits (*53, 148, 189, 211*). One property was operated commercially for a short time, but operations were discontinued because of low recovery. Early Bureau investigations showed that the rutile occurred in small needlelike particles, and good recovery was not accomplished by tabling, magnetic separation, or flotation. A concentrate containing 91 to 92 pct TiO_2 was produced, but recovery was only 12 to 17 pct. Later investigations were made on material from this deposit with the objective of maximizing total recovery of titanium and associated columbium in a lower grade concentrate. Reported investigations indicated that at least 50 pct recovery could be achieved by gravity methods.

Recovery of titanium and columbium was also investigated from another Arkansas deposit in which the primary titanium mineral was brookite (crystal modification of TiO_2). Samples contained about 6 pct TiO_2 and 0.13 pct Cb. Gravity methods were not effective because of intimate association of minerals. Flotation was effective when the material was ground to minus 150 mesh and deslimed. Recoveries of 69 pct TiO_2 and 80 pct Cb were made in a concentrate containing 94 pct TiO_2 and 2.4 pct Cb. It was expected that higher recoveries could be achieved in lower grade concentrate.

Investigations on samples of other deposits containing rutile and anatase (crystal modification of TiO_2) gave predictable results (*52, 208*). When minerals could be liberated only by grinding to minus 100 or minus 200 mesh, only flotation techniques gave good recovery; wet-gravity methods were not effective.

Massive Deposits Containing Ilmenite and Titaniferous Iron Minerals

Almost 30 pct of present titanium reserves occur in massive Ti-Fe deposits, and large amounts of subeconomic resources occur in this form. Titaniferous iron deposits also represent a significant iron resource. Materials examined by the Bureau averaged 1 to 20 pct TiO_2 and 7 to 65 pct Fe, and some samples also contained potentially recoverable manganese, vanadium, and zirconium (*6, 21, 42-43, 54-55, 58, 93, 171, 180, 188, 201, 205-206, 216, 219*).

Titanium and iron could be concentrated together to a degree from most materials tested but could not be effectively separated from each other. Titanium is somewhat soluble in magnetite and hematite, and some titanium remains in the iron minerals even in ores in which some ilmenite is separately mineralized. In the latter cases, an upgraded titanium concentrate could sometimes be made, but usually ilmenite and the iron mineral were too closely interlocked for clean separations to be effectively made by the methods used. As with other titanium materials, flotation was usually more effective than wet-gravity or magnetic methods for minus 100- and minus 200-mesh materials.

Separations were possible to a degree from some samples. Figures 8 and 9 show results of screening, stage grinding, and magnetic separation of two samples of Alaska titaniferous magnetite (*205, 216*). A Wyoming ore was beneficiated by a combination of low-intensity magnetic separation of titaniferous magnetite and electrostatic separation of ilmenite from olivine gangue, resulting in a concentrate averaging 46 pct Fe and 17 pct TiO_2 (*58*). Close sizing of feed to the electrostatic separation was required for good results. A titaniferous magnetite from Los Angeles County, CA, containing 2.1 pct TiO_2 and 6.5 pct Fe, was upgraded to a concentrate containing 25 pct TiO_2 and 39 pct Fe, with 72 pct TiO_2 recovery. Grinding, desliming, and flotation were used.

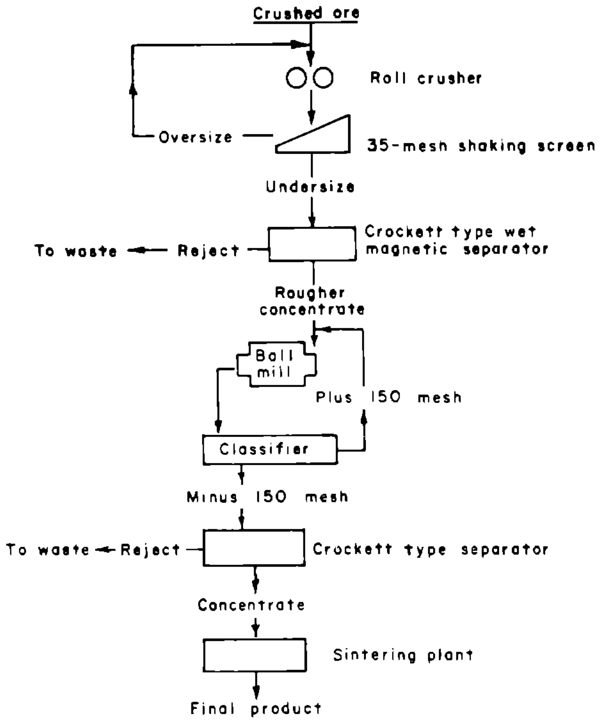

Figure 8.—Proposed flowsheet, Snettisham.

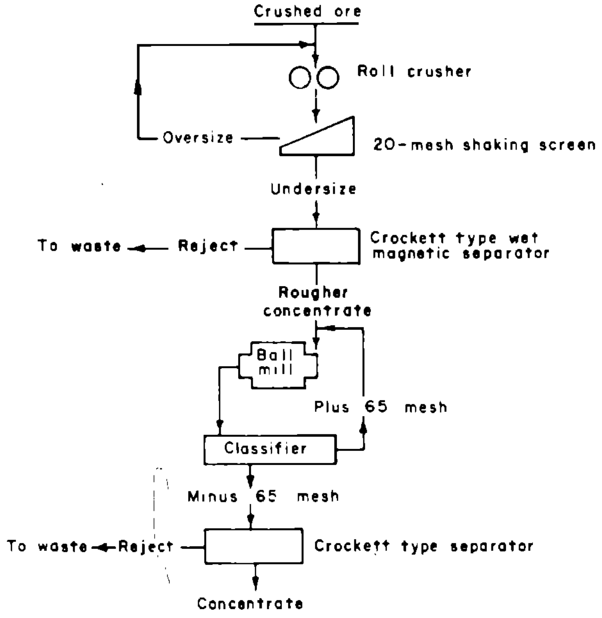

Figure 9.—Proposed flowsheet, Klukwan ore.

Summary of Physical Beneficiation Investigations

Most studies were exploratory rather than definitive, and many techniques remained untested. Most results were fairly predictable. Concentration of a given mineral depended on the degree to which it could be liberated in a large enough particle size for physical beneficiation methods to be effective.

Many early investigations had the objective of producing a high concentration of TiO_2 in the product, and total recovery was often low. Later studies showed that total recovery of titanium and also accessory minerals could usually be increased in a lower grade concentrate, thus indicating a direction for future test work.

CHEMICAL CONCENTRATION OF TITANIUM

High purity titanium metal can be produced by existing technology only from highly purified titanium compounds. All present titanium production is by reduction of titanium tetrachloride ($TiCl_4$), which is made by chlorinating relatively high-grade TiO_2 concentrate. Ores containing rutile can be physically concentrated to produce a satisfactory chlorination feed material, but ilmenite, titaniferous iron ores, and most other titanium source materials must be chemically treated to produce a sufficiently high-grade TiO_2 concentrate, which is often referred to as synthetic rutile. Chemical beneficiation is therefore necessary to recover titanium from most domestic resources. An important exception is the direct chlorination of high-grade ilmenite by E.I. duPont de Nemours & Co. to produce $TiCl_4$ for TiO_2 pigment production. This situation also exists in most other countries, many of which are developing methods for upgrading low-TiO_2 content materials. More than 90 pct of titanium raw materials are consumed in the manufacture of TiO_2 pigment (*3*, pp. 1123-1134; *108*, pp. 217-224, 1919-1926, 1951-1961, 1983-1987).

Many techniques have been proposed and patented for making rutile substitutes (*88, 142*). All processes are designed to separate titanium from iron, other valuable constituents, gangue materials, and chemical reactants or products that would interfere with chlorination. The Bureau has investigated some processes in considerable detail. Most procedures involve a number of different techniques, but they are categorized here according to the basic method used to separate other major material components from titanium.

Leaching Methods

Leaching methods are known in which TiO_2 in source materials is concentrated by selectively dissolving iron or other constituents. One such procedure for upgrading titaniferous iron ore has been studied by the Bureau (*149*). Iron was selectively reduced by roasting the ore with carbon, then removed by leaching with dilute sulfuric acid (H_2SO_4). This technique produced leached residues containing 2.1 to 2.8 times the titania content of the original ores and recoveries of up to 99.6 pct of the contained TiO_2. The problem of ferrous sulfate disposition from the leach solution remained unsolved, however, and other techniques have since been sought for processing these materials.

Leaching methods have been applied with more success to other titanium source materials. Titanium dioxide was dissolved from a red-mud-alumina process residue by mixing the residue with concentrated H_2SO_4, and heating and leaching with dilute H_2SO_4 solution (*63*). This material contained titanium in the form of perovskite and also contained relatively little iron. A titania product suitable for chlorination was precipitated from the solution. A similar procedure is currently being investigated at the Bureau of Mines Salt Lake City (UT) Research Center for recovering TiO_2, columbium, and rare earths from a perovskite concentrate (*184*). Up to 98 pct of the titanium in a Colorado perovskite concentrate was converted to water-soluble sulfate by digestion with concentrated H_2SO_4 solution at temperatures up to 300° C.

Leaching methods have been studied for upgrading titanium chlorination process residues for recycle (*135*). Residue samples contained, in addition to titanium and unreacted carbon, valuable elements such as columbium, chromium, vanadium, and zirconium that are eliminated from the feed material along with iron during chlorination. These elements were moderately to highly soluble in water, and the water leach residue containing most of the TiO_2, carbon, and silica was successfully chlorinated in laboratory tests. These studies are being continued, and methods for recovering the dissolved values from solution are currently being investigated.

Leaching methods for recovering titanium and other values from euxenite have also been investigated (*183*). Rare-earth columbates and titanates were converted to water-soluble compounds by fusion with ammonium sulfate or bisulfate. Calcination of the fusion product rendered the non-rare-earth constituents insoluble, thus permitting selective leaching of the rare-earth components.

Selective Volatilization of Iron

Removal of iron from ilmenite as ferrous or ferric chloride vapor is an alternative separation technique to leaching that offers possibilities for collecting the iron in a more usable form. Several processes have been proposed for converting the iron to $FeCl_2$ or $FeCl_3$ by reacting the ore with HCl gas or chlorine at 600° to 1,600° C (*88*). Some of these processes provide for recovery of iron, either as the metal or ferric oxide.

The Bureau has investigated an alternative process in which the iron in ilmenite was converted to iron pentacarbonyl, $Fe(CO)_5$ (*210*). The iron in the ore was first reduced to the metallic form. The catalyzed carbonylization reaction proceeded at temperatures of 110° to 130° C, lower than required for the formation of iron chlorides, and at carbon monoxide pressures of 1,000 lbf/in^2 and higher. The $Fe(CO)_5$ product can be decomposed to produce iron and obtain the carbon monoxide for recycling. This procedure is similar to a process that has been developed to extract nickel, iron, and cobalt as carbonyls (*168*).

Roasting and Sintering Methods

Roasting and sintering procedures have been used to cause solid-state reactions in ilmenite and titaniferous iron ores that result in separation of titanium and iron into different phases (*88*, pp. 4-5, 16-18). These phases can then be physically or chemically separated.

The Bureau has made extensive investigations of procedures in which titaniferous ores were roasted at about 1,050° C with carbon and sodium carbonate and the resulting metallic iron was effectively recovered by grinding and magnetic separation (*129-130, 149*). Use of sodium carbonate as a fixing agent gave a purer iron product than was otherwise obtained. Vanadium and other constituents reported to the titaniferous phase and were recovered by a series of roasting, leaching, and precipitation procedures. Titanium was recovered as TiO_2 by baking the chemically upgraded material with concentrated H_2SO_4, leaching with water, and precipitating the hydrated oxide. A proposed flowsheet for recovering titania, iron, vanadium, silica, and alumina products from titaniferous iron ores is outlined in figure 10. For ores in which only titanium and iron recovery is feasible, a simplified process is outlined in figure 11. A similar procedure was successfully applied to a titaniferous bauxite processing residue (*129*).

Investigations were also made on a process by which low-iron rutile was reported to have been made by roasting ilmenite with pyrite (FeS_2) and coke or coal at 650° to 900° C for 0.5 to 2 h. The rutile grains were then separated from the globules of sulfur and the hydrated iron oxides by physical methods (*206*). In Bureau tests, only 30 pct of the iron was separated from ilmenite concentrates by this method, and this approach has not been pursued.

Smelting Methods

Smelting, a process in which iron is reduced to metal under slagging conditions, has been the subject of continuing Bureau research efforts to separate titanium from titaniferous iron materials. Methods have been developed to produce pig iron and titaniferous slags in separate liquid phases and recover a TiO_2 concentrate or synthetic rutile from the slag.

Smelting is a promising method for recovering titanium and iron from titaniferous iron materials because it is already a standard process for producing iron. Slags containing recoverable titania for use in the sulfate pigment process have been produced in Canada since 1950.

Iron has been produced from titaniferous iron ores since the early days of the Catalan forge (*4*). Perceived problems, including a need for more reducing agent and difficulty in maintaining fluid slag, hindered acceptance of these materials as iron sources in the modern blast furnace. More recently, however, factors that increase slag viscosity have been identified, and methods for maintaining slag fluidity in electric furnaces have been developed (*88*). Slag becomes viscous as ferrous oxide (FeO) content decreases and as TiO_2 is reduced to lower oxides such as Ti_2O_3. Injecting oxygen into the slag can retard TiO_2 reduction, and retention of some FeO in the slag maintains low viscosity. Also, prevention of refractory titanium compound formation, such as carbide or nitride, is more effective in electric-arc furnaces than in the blast furnaces used in early investigations. Consequently, the Bureau has made extensive investigation using electric arc furnace smelting of domestic titaniferous iron-containing materials (*12, 62, 93, 140, 194*).

Basic thermodynamic studies of ilmenite reduction reactions were reported in 1946 (*185*). Ilmenite can be reduced effectively by carbon, as shown in reaction 1, but not by carbon monoxide:

$$FeO{\cdot}TiO_2 + C \rightarrow Fe + TiO_2 + CO, \qquad (1)$$

$$2\,CO \leftrightarrow CO_2 + C. \qquad (2)$$

At smelting temperatures, the equilibrium of reaction 2 is such that very little CO_2 is produced. Consequently, the stoichiometry of ilmenite reduction is essentially given by reaction 1. In practice, the amount of reductant required has varied from less than the stoichiometric amount to significantly more, depending on the smelting method used, efficiency of the process, and amount of FeO retained in the slag.

The effects of type and quantity of carboniferous reductant, fluxing agents, iron content of slag, and furnace liners on smelting temperature, slag separation and fluidity, and energy consumption were studied. In general, use of excessive reductant gave increased TiO_2 content and decreased FeO content of the slag, increased carbon content of the pig iron, increased smelting temperature and energy consumption, and increased slag viscosity. Requirements for fluxing agents to improve slag fluidity varied with different feed materials. Carbon furnace liners tended to have a reducing effect in the process, but other lining materials such as magnesite tended to contaminate the slag. In electric-arc smelting, relatively low voltages must sometimes be used because of the relatively high conductivity of titaniferous slags (*140, 222*).

A series of tests was made on samples with a wide range of titanium and iron contents and gangue compositions that represent several hundred million short tons of source materials[6] (*140*). Smelting conditions were found for each sample that produced pig iron satisfactory for steelmaking. Low-grade reductants such as bituminous coals, charcoal, and coke breeze were generally effective, and for most materials, energy, electrode, and furnace liner consumption were not considered to be excessive for this type of process. Slag compositions varied considerably, particularly in calcium and magnesium oxide content; these impurities would interfere with continuous chlorination and therefore must be eliminated before $TiCl_4$ can be produced from these materials.

Variations of smelting techniques include sodium borate smelting (*11, 69, 71*) and soda ash smelting (*70, 170*). Regarding the sodium borate smelting, investigations at the Bureau's Reno (NV) Metallurgy Research Center resulted in development of a technique for treating ilmenite to produce a low-iron sodium titanate from which titania pigment can be made by the conventional sulfate method without the usual formation of the waste material ferrous sulfate. Using an ilmenite concentrate from New Jersey beach sand (61 pct TiO_2), a titanate product containing 87 pct TiO_2 and less than 1 pct Fe was produced. The borate smelting process is outlined in figure 12 (*11*).

With this proposed process, ilmenite, coal, and sodium borate are smelted at 2,200° F in an electric furnace to produce pig iron and a borate-titanate slag containing approximately 40 pct TiO_2. More than 90 pct of the iron is recovered as marketable pig iron; about 99 pct of the titanium is contained in the slag.

Molten slag is tapped into a leach tank containing dilute sodium borate solution, resulting in quenching and granulation of the slag. The quench-granulation tank is the first of a three-stage countercurrent leach system,

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[6] Including ilmenites, titaniferous magnetites, and one sample of perovskite.

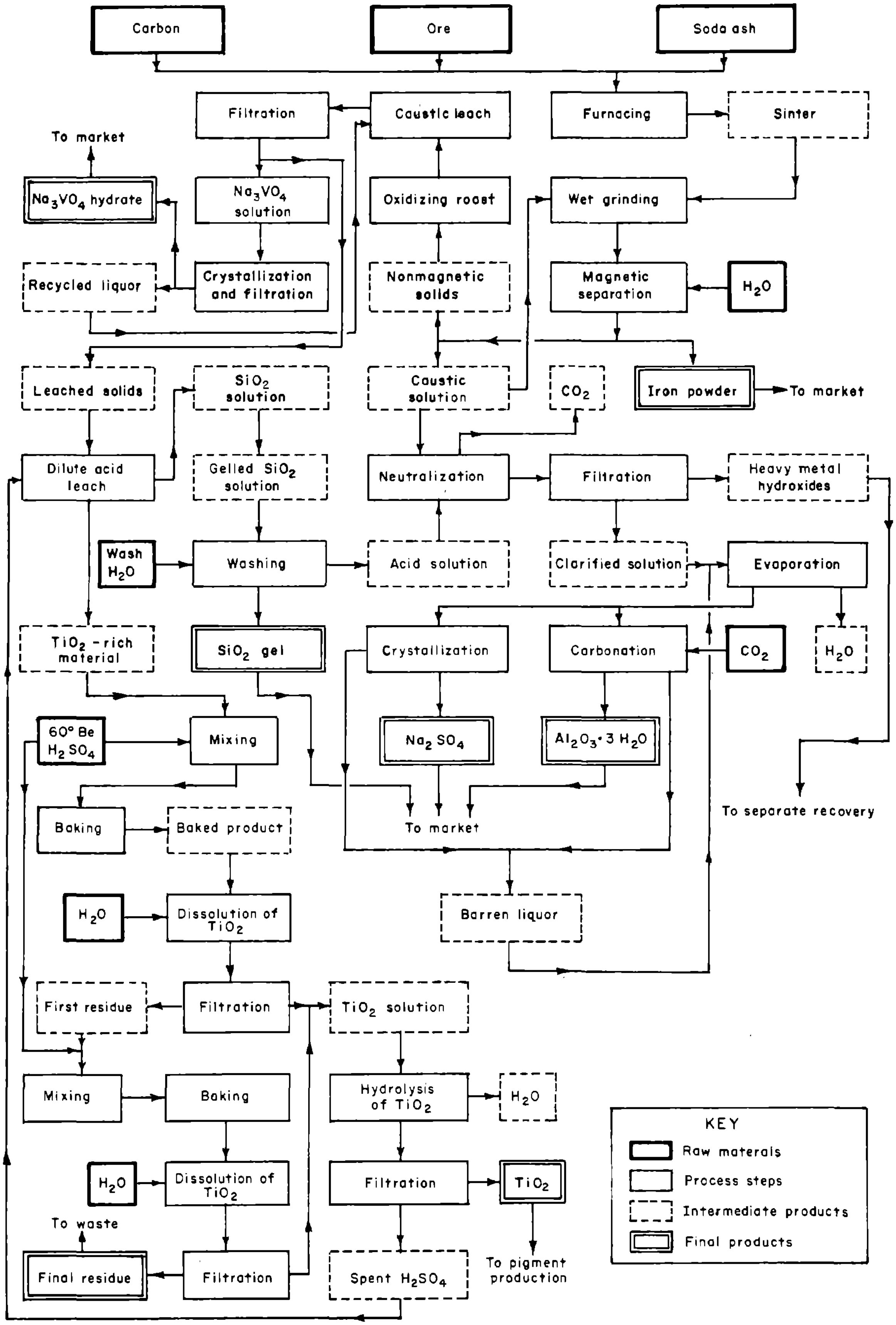

Figure 10.—Revised flowsheet for Tahawus ore.

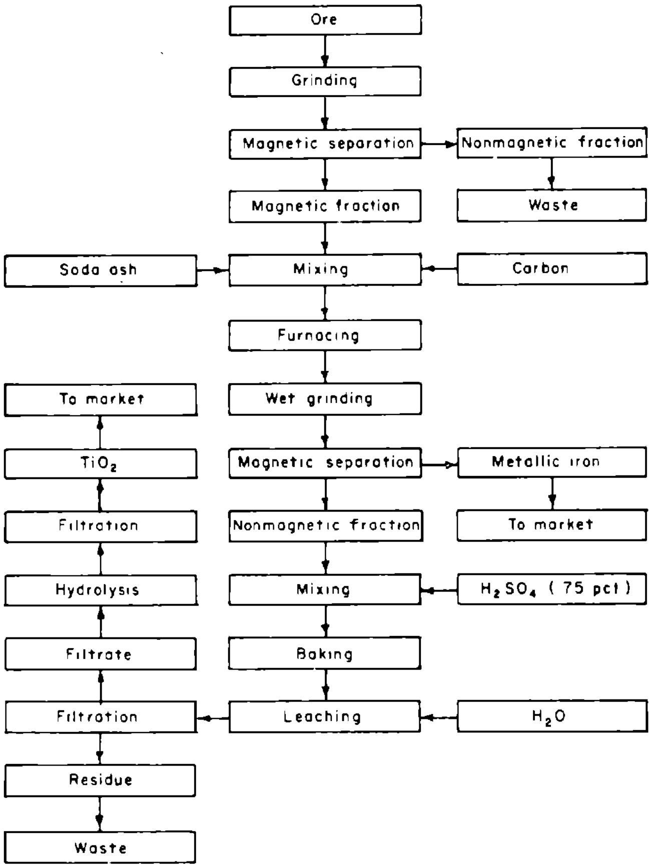

Figure 11.—Simplified flowsheet for Rhode Island ore.

each stage made up of an agitator and thickener. The thickened slurry from the third stage, containing 99 pct of the titanium in the slag feed, is filtered and dried.

The filtrate is returned to the third leach stage. Overflow liquor from the first stage leach is mixed with sodium carbonate to replace sodium lost in the smelting reaction and treated in vacuum crystallizers at 86° F. The sodium borate crystals are separated from the liquid with a centrifuge. Wet sodium borates are partly dehydrated by calcining at 1,500° F, then fused at 1,800° F. The molten borates are solidified, crushed, and recycled to the smelting operation. The two-stage dehydration step is necessary to avoid formation of an extremely fine, fluffy powder that is difficult to handle.

The Bureau also has investigated a soda-smelting technique for processing ilmenite into pig iron and a titanium slag that is suitable for a feed to a sulfate-process titania pigment plant. By this procedure, the generation of ferrous sulfate waste and its associated disposal problem is obviated. Molten titania slag was quenched, water leached, and filtered to yield a sodium titanate intermediate product containing about 70 pct TiO_2, 1 pct Fe, and 20 pct Na_2O. This intermediate product, high-soda titanate (HST), was mixed with H_2SO_4, calcined, quenched, and water leached to produce a low-soda titanate (LST) product that contained only 2 pct Na_2O. Both the HST and LST were evaluated as feed materials for preparing titania by the sulfate process.

This investigation has shown that HST and LST can be utilized effectively as a substitute for an ilmenite feed in the sulfate process for preparing titania. Digestion with 50 pct H_2SO_4 resulted in extracting over 95 pct of the available TiO_2 from these titanates. The resulting pregnant solutions containing 164 to 200 g/L TiO_2 can be hydrolyzed to yield a high-purity titania precipitate, which represents about 95 pct of the TiO_2 in the pregnant solutions.

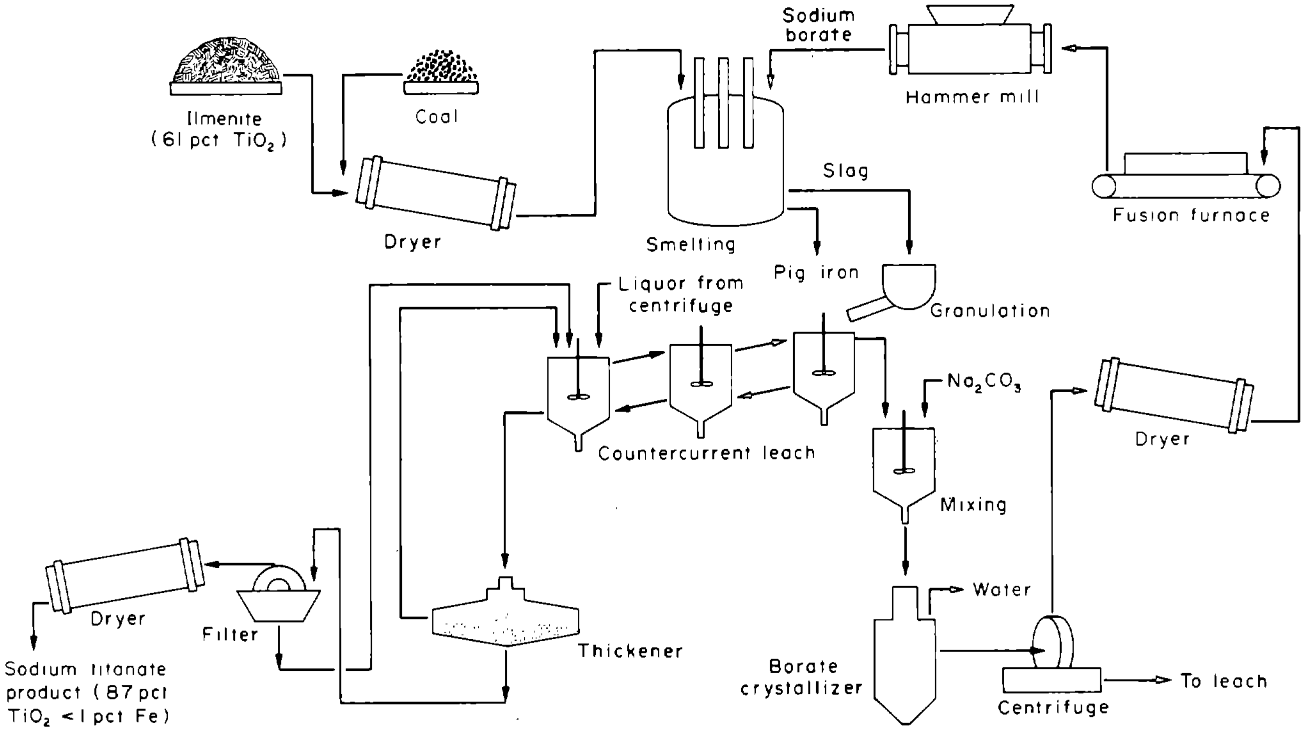

Figure 12.—Borate smelting.

Barren H_2SO_4 solutions that result when HST is digested with strong H_2SO_4 can be reconcentrated by electrodialysis and those that result when LST is digested can be reconcentrated by vacuum-thermal evaporation. Regenerated acid can be reused in digesting additional titanate to prepare titania without a significant increase of impurities in the product. Both acid regeneration methods studied in this investigation are energy intensive, and the use of regenerated acid appears uneconomical when compared with the cost of virgin H_2SO_4.

Improvements in the basic smelting procedure also have been developed. When titaniferous iron sands that had been prereduced commercially were smelted, benefits included greater concentration of TiO_2 in the slag, lower concentration of alkaline-earth oxides in the slag, lower electrical energy consumption, and lower electrode consumption (*138*). Injecting most of the carbon reductant directly into the melt instead of mixing it all with the ore or concentrate resulted in improved carbon utilization when the reductant did not contain a high percentage of volatiles and ash (*139*). Emission of airborne effluents was also reduced. The effectiveness, economics, and limitations of the smelting process have therefore become well established.

A matte smelting method was investigated for separating titanium and associated columbium and manganese as sulfides rather than oxides (*148*). Pyrite (FeS_2) and coke were heated with an ilmenite concentrate, and metallic iron and a mixed sulfide matte were produced, based on the following reactions:

$$\mathrm{FeS_2} \xrightarrow{\Delta} \mathrm{FeS} + \mathrm{S} \tag{3}$$

$$\mathrm{FeS} + (\mathrm{Ti,Cb,Mn,Fe})\mathrm{O} + \tfrac{1}{2}\,\mathrm{C} \rightarrow (\mathrm{Ti,\ Cb,\ Mn})\mathrm{S} + \mathrm{Fe} + \tfrac{1}{2}\,\mathrm{CO_2} \tag{4}$$

Reaction 3 proceeds at temperatures above 900° C. In Bureau studies, titanium and columbium were separated in a sulfate matte, but efforts to convert the matte into a product that could be chlorinated were not successful, and this technique therefore has not been pursued.

Two generally applicable methods have been developed for upgrading titaniferous slags that contain calcium, magnesium, or manganese oxides. These materials cannot be directly chlorinated because liquid chlorides of these impurity elements form, and accumulate in the chlorination reactor. In one method, molten slag was treated with oxygen and titanium pyrophosphate (TiP_2O_7) to convert lower titanium oxides and calcium titanate to TiO_2 (*49, 92*). The solidified treated slag contained rutile crystals in a glassy matrix that contained most of the unwanted elements. The matrix was separated from the crystals by grinding, dissolution in dilute H_2SO_4 solution, and mechanical abrasion. This process was most successful when applied to slags that contained 5 pct or less FeO and 60 pct or more TiO_2. A rutile product was made that contained 88 pct TiO_2, and represented 88 pct recovery of the TiO_2 in the slag. The proposed process is outlined in figure 13. A cost analysis for this process, based on 500 st/d production, indicated that the product would be competitive with natural rutile concentrate. Electric power requirement of 4,295 kW·h/st of rutile product would indicate the need to locate the plant where electricity is plentiful and inexpensive.

A second slag treatment method converts calcium, magnesium, and manganese oxides to soluble sulfates that can be leached with water or dilute HCl solution (*3, 48, 51*). Pelletized slag containing sodium sulfate or sodium carbonate, which acted as sulfation promoters, was reacted with sulfur trioxide or a mixture of sulfur dioxide and oxygen at 600° to 1,100° C, then leached with 1-pct HCl solution to remove the impurities and additives. This procedure lowered the impurity oxide content of the slag to well below 1 pct. This method was, as the one discussed previously, most effective for slags containing less than 5 pct FeO. Conversion of magnesium and manganese species to sulfates depends on transformation of the pseudobrookite structure in the slag to rutile, in which the magnesium and manganese oxides are much less soluble, and high levels of FeO tend to stabilize the pseudobrookite even under high oxygen pressure.

Investigations being continued in the area of smelting and slag treatment include studies of the effects of various catalysts and reductants in prereducing ilmenite and the possibility that these catalysts can also serve as sulfation promoters in slag treatment.

Methods have been studied for recovering some accessory mineral values in titaniferous materials using smelting procedures. Vanadium recovery from iron ores was a subject of considerable interest as early as the 1930's. In early Bureau investigations using a blast furnace, vanadium was recovered in the pig iron (*221*). Later tests using an electric furnace showed that most of the vanadium could be separated in the slag by avoiding the conditions necessary to reduce vanadium (*194*). A method was developed for recovering vanadium from titaniferous magnetite before smelting by roasting the ore at 950° C with sodium carbonate (*6*). The calcine was then leached with water, and vanadium was recovered from the solution by precipitation. Ninety percent of the vanadium was recovered using this procedure.

Smelting tests on an Idaho ilmente containing manganese and columbium showed that these elements tended to become concentrated in the slag and that manganese tended to replace iron in the slag (*12*).

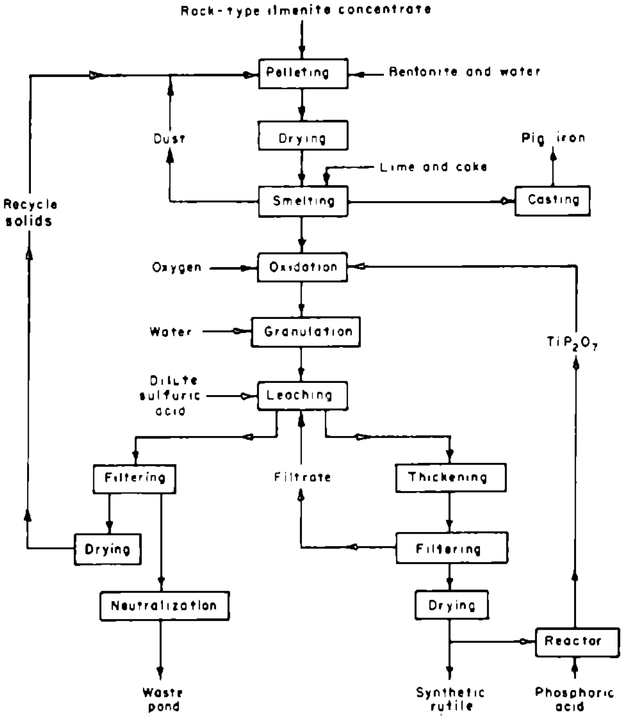

Figure 13.—Production of synthetic rutile from ilmenite.

Summary of Chemical Concentration Investigations

Methods have been demonstrated for recovering TiO_2 concentrate and pig iron from representative samples of domestic titaniferous iron source materials. These methods are technically feasible and should, in the foreseeable future, become economically attractive. Development of these resources could become inspired by increased prices or more limited availability of imported titanium and iron raw materials and also by demonstration of a more economical process for producing titanium from titanium compounds or concentrates.

PREPARATION OF TITANIUM INTERMEDIATE COMPOUNDS

All titanium found in nature is in the form of impure oxides, and all processes for producing the metal therefore involve separation of impurities and oxygen. Titanium source materials are processed into a purified intermediate compound from which the metal is produced. Because the oxides are very stable, direct reduction to produce titanium is difficult, and procedures investigated to date produce relatively impure metal at best. In more successful processes, an oxygen-free titanium compound is first produced and this compound is then reduced to metal.

A number of chemical routes from impure titanium oxide to purified metal are outlined in figure 14 (*89*). To guide the development of conceptual processes based on these routes, the Bureau has collected and developed basic thermochemical data for the corresponding reactions (*104-106, 109, 217*). Processes based on a number of these routes have been examined. The various degrees of success attained have been determined by the thermodynamic favorability of the process and the physical nature of the reactants, intermediates, and final products.

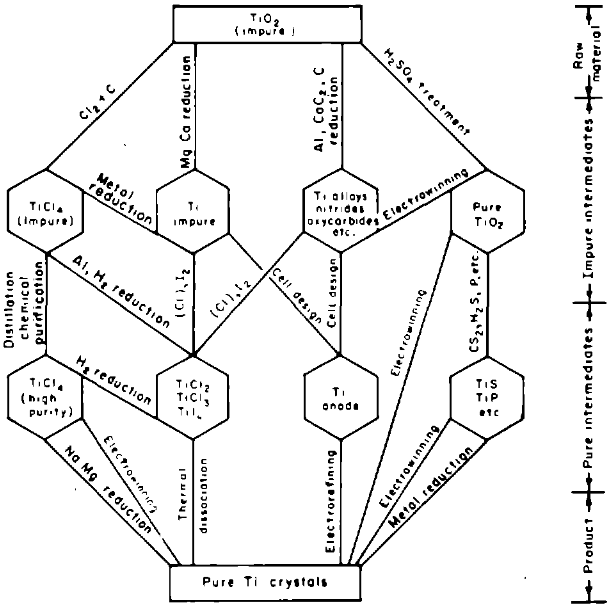

Figure 14.—Possible routes for titanium processing.

PURIFIED TITANIUM DIOXIDE

Direct production of titanium metal from TiO_2 is an attractive prospect because two commercial processes already exist for preparing high-grade TiO_2 (*126, 136*). The process formerly used to produce most U.S. TiO_2 pigment and still used to produce about 60 pct of the world's TiO_2 pigment consists of dissolving ilmenite or high-TiO_2 slag by digestion in concentrated H_2SO_4, removing some of the iron by precipitation as hydrated $FeSO_4$, precipitating hydrated TiO_2, filtering and calcining the precipitate, and grinding the TiO_2 calcine. In a process becoming more common for pigment production, rutile, synthetic rutile, high-TiO_2 slag, or an ilmenite-leucoxene-rutile mixture is chlorinated and $TiCl_4$ is separated, purified, and converted to TiO_2. The latter process could economically use lower grade titanium materials than are presently treated if the waste material, $FeCl_3$, produced were dechlorinated and the chlorine recycled.

The Bureau has investigated the applicability of the commercial H_2SO_4 digestion process to two other potentially important types of titaniferous materials: titaniferous slags from domestic ilmenite, and perovskite. Slags generally contain less iron than ilmenite or titaniferous iron ores but may contain significantly more silicon, aluminum, calcium, magnesium, and sodium oxides, depending on the process used to produce them (*6, 129-130*).

These impurities inhibited the recovery of titanium in H_2SO_4 digestion. Silica tended to form bulky residues that retained large amounts of liquor and filtered poorly. Aluminum and sodium tended to form salts that resulted in supersaturated, unstable solutions. Magnesium combined with titanium in the slag and rendered it less soluble.

Two technologies were developed to remove the troublesome impurities from slags containing titanium as TiO_2. In one method, the slag was mixed with enough 60-pct H_2SO_4 to react stoichiometrically with the sodium, aluminum, and iron but not with titanium. The mixture was baked to fumes of SO_3 to ensure dehydration of silica, then leached with 5-pct H_2SO_4 solution at the boiling point. This procedure removed 80 to 90 pct of the sodium, aluminum, and iron and less than 5 pct of the titanium. Filtration of these solutions was difficult, however, because of finely divided TiO_2 and bulky SiO_2 residue. The second method was more effective. Leaching with 15 to 20 pct H_2SO_4 solution at ambient temperature removed sufficient sodium, aluminum, and iron oxides and also up to 90 pct of the SiO_2. Proper control of temperature, liquid-solid ratio, and quantity of H_2SO_4 produced a solution that did not gel in the time needed for solid-liquid separation by settling, decantation, and filtration. A preliminary oxidizing roast at 800° to 900° C lowered acid requirements, reduced titanium extraction, and improved settling characteristics in the subsequent slag purification leach. Recovery of pigment-grade TiO_2 by H_2SO_4 digestion was made by essentially the same procedure used in pigment manufacture (*130*).

High-grade TiO_2 was also recovered by similar procedures from slag in which titanium was present in forms other than TiO_2. Slag derived by smelting ilmenites with sodium carbonate contained titanium as sodium titanates (*70, 170*). Soluble sodium compounds were removed by either leaching with water at 60° to 70° C or by heating with 36-pct H_2SO_4 at 500° C, then leaching with water at 70° to 80° C. Titanium dioxide products were obtained, as before, by H_2SO_4 digestion (*70*).

Based on results from slagging and sintering methods used, flowsheets have been outlined for recovering high grade TiO_2, pig iron, and other byproducts from titaniferous iron ores, two of which are given in figures 15 and 16. In these schemes, vanadium in the ores is recovered, and it seems likely that methods can be developed for

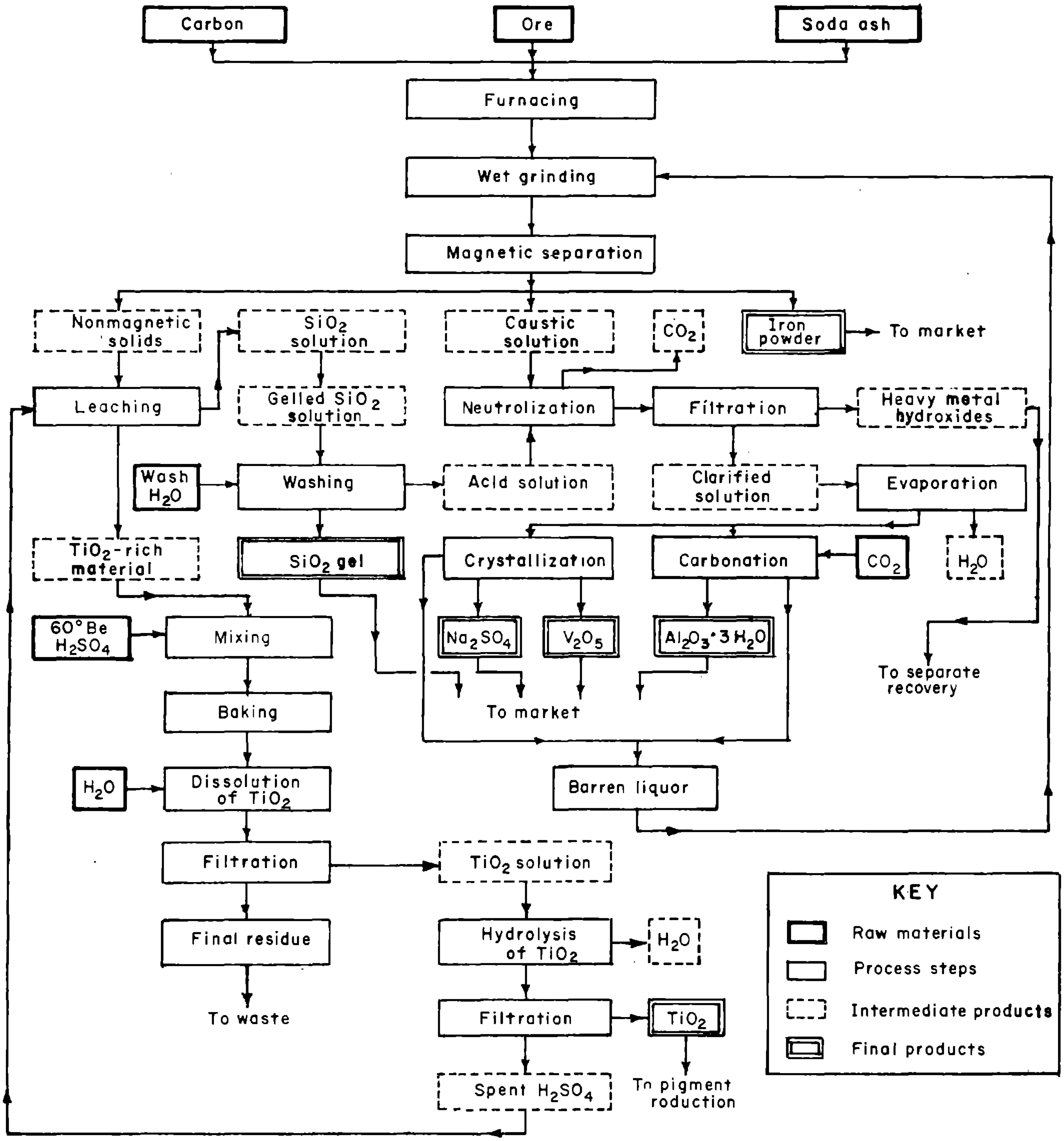

Figure 15.—Proposed flowsheet for recovery of titania, iron, and byproducts from titaniferous ores.

recovering other potential byproducts from different ores.

The H_2SO_4, baking method was also used to recover TiO_2 from a material containing titanium as perovskite (*63*). The material tested was an alumina production process residue containing 19 pct TiO_2, 30 pct CaO, and significant amounts of ferric oxide, silica, and alumina. Digestion was made with concentrated H_2SO_4 at temperatures up to 400° C. The product was then mixed with dilute H_2SO_4 solution, ferric iron was reduced to the less soluble ferrous state by adding scrap iron. The solution, which still contained significant concentrations of iron and aluminum, was seeded with TiO_2 and heated to hydrolyze the titanium. The resulting product contained approximately 95 pct TiO_2 and 2 to 5 pct Fe_2O_3 and was therefore not pigment-grade material, although it was suitable for chlorination. The Bureau, however, still has interest in producing high-grade TiO_2 by this procedure.

Titanium and other values were extracted from euxenite by a baking and leaching procedure (*183*). Euxenite concentrate was baked with ammonium sulfate or bisulfate at approximately 400° C for 3 to 4 h in an ammonia atmosphere. A water leach then extracted most titanium, columbium, tantalum, yttrium, and rare-earth oxides. Although recovery of these values from solution was not investigated in the original study, titanium would likely be recovered as an oxide. This technique may be a viable option to acid baking and leaching for some titanium source materials if the ammonium reagents can be recycled.

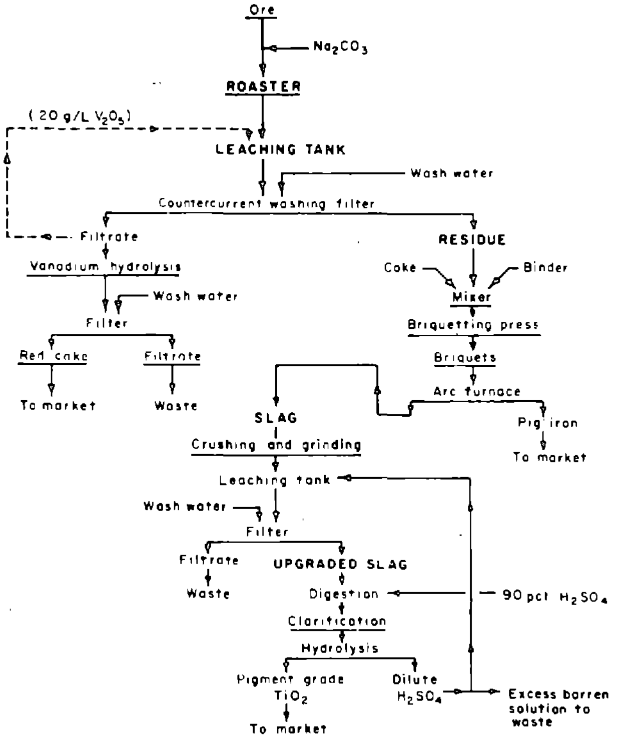

Figure 16.—Flowsheet for recovering iron, vanadium, and titanium from Iron Mountain ore.

CHAPTER 2.—TITANIUM TETRACHLORIDE

CHLORINATION HISTORY AND THEORY

Titanium tetrachloride ($TiCl_4$) can only be produced by a dry chlorination process, as it hydrolyzes rapidly in the presence of water. When pure, it is a colorless liquid with a specific gravity of 1.726 and boiling point of 136.4° C. It fumes readily in moist air to form TiO_2 and HCl. E. S. George first prepared $TiCl_4$ in 1825 by passing chlorine over titanium carbonitride. Dumas chlorinated a red-hot mixture of carbon and TiO_2 in 1826. Since then, numerous feed materials, including rutile, ilmenite, beneficiated ilmenites, synthetic rutile, titanium pigments, slags, and various titanium compounds such as nitrides, oxycarbides, and sulfides have been chlorinated. Chlorinating agents used have included sulfur dichloride, carbon tetrachloride, and phosgene, as well as chlorine. Carbon monoxide has been used as a reducing agent in place of carbon. A large number of patents have been issued covering equipment, charge preparation, chlorination procedures, and methods for condensation of the reaction products. Most commercial production today is accomplished by reacting a mixture of TiO_2 (usually in the form of rutile) and carbon directly with chlorine in fluid-bed reactors. The reactions involved are generally represented by the following:

$$TiO_2 + 2Cl_2 + C \rightarrow TiCl_4 + CO_2, \qquad (5)$$

$$TiO_2 + 2Cl_2 + 2C \rightarrow TiCl_4 + 2CO, \qquad (6)$$

$$CO_2 + C \rightarrow 2CO, \qquad (7)$$

$$TiO_2 + 2CO + 2Cl_2 \rightarrow TiCl_4 + 2CO_2. \qquad (8)$$

Reactions 5 and 6 are the principal net reactions that occur in a chlorinator. Reactions 7 and 8 are also involved in the system and can be added to yield 5 as a net reaction. Rowe and Opie (*181*) showed that reactions 5 and 6 were temperature dependent. The temperature effect was in a direction that would satisfy the $CO\text{-}CO_2$ ratio, based on the Boudouard equilibrium for reaction 7. Thus, production of CO is favored by higher temperatures. A study of reaction 8 by Dunn (*45*) indicated that CO may provide gaseous transport for oxygen from ore to carbon. Side reactions with oxides of impurity elements not only consume chlorine, but interfere with the chlorination operation when impurities are present in sufficiently large quantities. The melting, sublimation, and boiling points of some chlorides and oxychlorides that could be formed are shown in table 1.

Impurity elements, except silicon, aluminum, and trivalent iron, form chlorides that are not very volatile at the operating temperature. These less volatile chlorides melt and form coatings on the feed material particles, which reduces chlorination efficiency and causes sticking and agglomeration of the bed. The only volatile chloride that causes operating difficulties and requires special handling after leaving the reactor is ferric chloride.

Table 1.—Melting and boiling points of chlorination products,[1] degrees Celsius, at 1 atm

Compound	Melting	Boiling	Compound	Melting	Boiling
$AlCl_3$	[2]194	[3]182.7	$MgCl_2$	714	1.412
$CaCl_2$	782	1,600	$MnCl_2$	652	1,225
$FeCl_2$	670	[3]1,030	$SiCl_4$	−68	57.6
$FeCl_3$	306	315	$TiCl_4$	−23.5	136.4

[1] Langs Handbook of Chemistry, 11th ed., McGraw-Hill, 1973.
[2] 5.2 atm.
[3] 760 mm Hg.

When materials high in iron content are chlorinated, the following reactions in addition to reactions 5 and 8 become significant:

$$2FeO + C + 2Cl_2 \rightarrow 2FeCl_2 + CO_2, \qquad (9)$$

$$2FeCl_2 + Cl_2 \rightarrow 2FeCl_3. \qquad (10)$$

At temperatures below about 1,000° C, the equilibrium of reaction 10 favors formation of ferric chloride, whereas at higher temperatures, ferrous chloride is the more likely product.

The Kroll patent (*113*) for production of titanium by reduction of the chloride with alkaline-earth metals was issued in June 1940, and in October of that year, Kroll presented before the 78th general meeting of the Electrochemical Society (*114*) details of his experiments for reduction of $TiCl_4$ with magnesium metal. The Bureau of Mines, in 1940, decided to concentrate its research for production of ductile titanium on adaptations of the procedures described by Kroll. A primary requirement of the method was the availability of high-purity $TiCl_4$. Research on the production of $TiCl_4$ was carried out concurrently with the reduction research.

Methods for the production of $TiCl_4$ by the reaction of rutile with chlorine in the presence of carbon were well established in commercial practice for the production of TiO_2 pigment. Ilmenite, the only other titanium mineral of commercial importance, was not as promising a feed material because of the chlorine consumed in the formation of iron chlorides and the difficulty in treating the iron chlorides for recovery of chlorine. However, the Bureau investigated ilmenite as a feed material because of the scarcity of rutile in domestic deposits. Methods for partial removal of the iron were investigated, and the chlorination characteristics of the beneficiated products were determined.

PIGMENT PRODUCTION

By far the greatest requirement for $TiCl_4$ is as an intermediate in the manufacture of TiO_2 pigment. Relatively smaller quantities are used for metal production. Production of TiO_2 pigment in the United States in 1985 amounted to 860,000 st (480,000 st Ti content), while production of titanium sponge metal was around 23,000 st, representing a TiO_2 equivalent of about 38,000 st (*127*).

Titanium dioxide pigment is produced commercially by two methods, which require different raw materials. In the sulfate process, ilmenite or high-titania slag is reacted with H_2SO_4, a portion of the contained iron sulfate is crystallized and removed, and the titanium hydroxide is precipitated by hydrolysis, filtered, and calcined. In the chloride process, rutile is converted to $TiCl_4$ by chlorination at 850° to 900° C in the presence of petroleum coke. All U.S. commercial chloride-process plants use fluid-bed chlorinators, although static-bed systems can be used. Rutile is the preferred raw material for making $TiCl_4$, but ilmenite and some high-grade titania slags can also be used.

Titanium tetrachloride so prepared may be used either in making pigment or for reduction to metal. There is little difference in the specifications. In making pigment, the $TiCl_4$ is oxidized with air or oxygen, and the resulting finely divided TiO_2 is calcined at 500° to 600° C to remove residual chlorine and any HCl that may have been formed in the reaction. Aluminum chloride is added to the $TiCl_4$ to assure that virtually all of the titanium is produced in the rutile crystal form. Pigment plant recoveries of TiO_2 are approximately 89 pct for the chloride process and 80 pct for the sulfate process.

The sulfate pigment process is responsible for the major environmental problem in the titanium industry, generating up to 3.5 st (dry basis) of waste per short ton of product. Because of increased environmental concern, there has been a trend away from the sulfate process. Nearly all of the new or expanded TiO_2 pigment plant capacity installed since 1970 has been for the chloride process and a substantial tonnage of sulfate process capacity has been shut down.

Although the United States has large reserves of titanium in the form of ilmenite, nearly all U.S. sponge metal production has been derived from imported rutile and synthetic rutile. This heavy reliance on foreign concentrates has developed because most producers of $TiCl_4$ prefer rutile or synthetic rutile over ilmenite as a plant feed material because of its much higher titanium content and absence of iron. U.S. rutile produced in Florida has not been used for metal production because of the high cost of shipping it to plants where tetrachloride for metal production is made. The Kerr-McGee Chemical Corp. synthetic rutile plant in Mobile, AL, lowers dependence on imported rutile, but this plant uses Australian ilmenite as feed material and the synthetic rutile made there has not yet been used extensively for metal production. Australian ilmenite is obtained at relatively low cost compared to domestic ilmenite and processes better by the Kerr-McGee system.

LABORATORY STUDY OF CHLORINATION VARIABLES

A laboratory study of the comparative chlorination characteristics of various titanium-bearing materials was undertaken by the Bureau at Boulder City, NV, to determine the effects of operational variables on the efficiency of TiO_2 chlorination and chlorine usage. Commercial materials investigated were ilmenite and rutile concentrates, a titanium enriched slag, and Titanox (a minus 200-mesh, 97.5-pct TiO_2 pigment product).

The chlorination apparatus was a standard combustion tube furnace containing a 1-in-ID, 30-in-long Vycor tube. The charge to be chlorinated, 9 to 12 g, was placed in a silica combustion boat and positioned near the center of the furnace. The system was purged with helium as the furnace was heated to the chlorination temperature. When chlorination temperature was attained, chlorine gas was added at a constant rate in a quantity approximately equal to the stoichiometric requirement for converting the titanium and iron to their respective chlorides. At the conclusion of chlorination, the furnace was swept with helium until the charge cooled to room temperature. The residue was analyzed for iron and titanium, and reaction efficiencies were calculated.

The laboratory test procedure, though differing in many respects from the features in commercial chlorinators, was valuable in deriving comparative data. In the laboratory, the chlorine was passed over the surface of the charge. The results, which averaged over 90 pct reaction efficiency for tests made under optimum conditions, demonstrated that adequate contact was attained. The temperature of the reaction in the laboratory tests was undoubtedly under better control than could be attained in commercial reactors, and this factor improved reproducibility of the data.

Exploratory tests were made using commercial pigment material (Titanox) to determine the characteristics of the apparatus and to establish practical limits of the variables. Chlorination temparatures varied from 450° to 750° C, while chlorine feed rates were from 1.40 to 4.00 $cm^3/(min \cdot cm^2)$. Reaction efficiencies increased rapidly as temperatures were increased to 650° C and increased at a lower rate through 750° C. Reaction efficiency decreased with increasing chlorine feed rate. Three reducing agents, charcoal, graphite, and petroleum coke, were used with Titanox. When minus 200-mesh material was used, all were satisfactory, but the charcoal consistently gave reaction efficiencies several percentage points higher than the other two materials. Tests on the effect of particle size of charcoal used as a reducing agent showed that reaction efficiency dropped off very sharply when the particle size was increased from minus 65 plus 200 to minus 28 plus 65 mesh. Theoretical carbon requirements for converting the oxygen in the titania to CO and CO_2 are 30 and 15 pct, respectively. When the carbon was less than 15 pct of the TiO_2, reaction efficiency was low. When the carbon was in excess of 30 pct, there was no adverse effect on chlorination efficiency. Charges containing 24 to 28 parts of carbon per 100 parts of TiO_2 gave the maximum chlorination efficiency.

The analysis of four commercial materials tested in the tube furnace are shown in table 2.

Table 2.—Analysis of titanium-bearing materials treated in tube chlorinator, percent

	TiO_2	FeO	SiO_2
Pigment	97.5	ND	ND
Rutile	89.5	4.01	1.54
Slag	69.9	9.75	3.60
Ilmenite	55.0	30.5	6.73

ND Not detected.

Each of the materials was chlorinated at two temperatures, 700° and 800° C; at three chlorine feed rates, 1.4, 2.8, and 4.7 $cm^3/(min \cdot cm^2)$; and as loose and compacted charge. In addition, the ilmenite, rutile, and slag were tested as separate-sized fractions of minus 200 mesh, minus 100 plus 200 mesh, minus 65 plus 100 mesh, minus 48 plus 65 mesh, and as a composite of these sizes. The titanium pigment was finer than minus 200 mesh as received. Carbon ratios, as a percent of the titanium-bearing material, were ilmenite, 22; rutile, 30; slag, 26; and pigment, 30. Carbon was minus 200 mesh.

For all of the materials, the highest chlorination efficiency was obtained at the highest test temperature. There was a 2-pct average drop in titanium chlorination efficiency as the chlorine feed rate was increased from 1.4 to 2.8 $cm^3/(min \cdot cm^2)$, but in some tests the efficiency was higher for the higher chlorine feed rate. Titanium chlorination efficiency dropped markedly when the rate was increased to 4.7 $cm^3/(min \cdot cm^2)$ and averaged 12 pct lower than for the 2.8 $cm^3/(min \cdot cm^2)$ tests. Titanium chlorination efficiency decreased with an increase in particle size of the titanium-bearing material. However, a composite sample of all screen sizes (minus 48 mesh) chlorinated almost as well as minus 200-mesh material. No significant differences in chlorination characteristics were observed between loose and pelletized charges. Comparative reaction efficiencies for the four materials are given in table 3. The data represent the results obtained at 800° C with a 1.4 $cm^3/(min \cdot cm^2)$ chlorine feed rate.

Table 3.—Reaction efficiencies for various titanium-bearing materials, percent

Material	TiO_2 reacted	FeO reacted	Cl_2	
			Reacted	Used in $TiCl_4$
Pigment	93	NAp	96	96
Rutile	94	91	99	96
Slag	90	91	99	94
Ilmenite	90	95	91	68

NAp Not applicable.

CHLORINATION OF TITANIUM DIOXIDE MATERIALS

Chlorination studies have been made by the Bureau of Mines on a variety of materials containing TiO_2. These include rutile concentrates, synthetic rutile, titaniferous slags, and chlorination process residue. Titanium tetrachloride is produced at temperatures of 700° to 900° C when chlorinating these materials and therefore $TiCl_4$ and many byproducts such as $FeCl_3$ and $SiCl_4$ are formed as gases.

Production of $TiCl_4$ by the chlorination of rutile concentrates was commercially established by the 1950's and the thrust of the Bureau of Mines has therefore been to investigate application of the established techniques to alternative materials. Most studies were made on titaniferous slags. Early tests using upgraded slag containing 74 pct TiO_2 showed that this technique was very promising (*6*). More than 99 pct of the contained titanium was converted to $TiCl_4$ when two parts of minus 200-mesh slag were mixed with one part coke and contacted with chlorine at 700° to 800° C.

More extensive tests were made to determine the chlorination characteristics of high-titanium slags made by arc-furnace smelting of an ilmenite concentrate produced as a byproduct of a monazite dredging operation in Idaho (*15, 178*). Laboratory tests were made to determine carbon requirements and to study the effect of particle size and temperature upon chlorination. Preliminary tests tentatively established the lowest practical chlorination temperature to be 480° C. Based on the results of these tests, a 4-in vertical-shaft, fixed-bed chlorinator was constructed, and chlorination studies were conducted on several types of slag produced at the Bureau of Mines laboratory in Albany, OR, on a commercial slag, and on untreated Idaho ilmenite.

Analytical data for the titaniferous materials used in these studies are shown in table 4.

Table 4.—Analytical data for titaniferous materials used in chlorination studies, percent

Material	TiO_2	Fe	Mn
Air-cooled Idaho slag:			
Sample 1	81.7	7.7	4.3
Sample 2	87.4	2.6	7.4
Vacuum-cooled slag	78.2	7.2	4.0
Water-quenched slag	88.9	2.6	5.6
Vacuum-cooled slag, ignited at 800° C	75.4	6.5	4.7
Water-quenched slag, ignited at 800° C	79.1	2.3	4.6
High-manganese, low-iron slag	86.7	2.4	7.1
Quebec slag	71.4	11.2	.8
Idaho ilmenite concentrate	39.4	33.1	3.0

Carbothermic reduction of ilmenite in the electric furnace proceeds to a varying degree depending on the amount of carbon added and the temperature attained in the smelting operation. The total titanium content of the slag is reported as equivalent TiO_2, although lower titanium oxides, such as Ti_2O_2, are present.

Oxidation of the lower titanium oxides probably occurs during cooling of slags in air. Because an oxidized slag might chlorinate with less vigor than a highly reduced slag, several slag taps were cooled under controlled conditions for chlorination tests.

A 500-lb slag button was placed in a large steel bell jar and allowed to cool under a reduced pressure of 5 mm Hg. This was designated vacuum-cooled slag. In a further effort to halt any air oxidation of the slag during cooling and, at the same time, to cause fragmentation of the slag to facilitate subsequent crushing, a tapping of slag was put under a spray of water as soon as it could be moved from the furnace area. This was termed water-quenched slag. Portions of the water-quenched and vacuum-cooled slags were crushed to minus 200 mesh and ignited at 800° C for 72 h. These were designated water-quenched, vacuum-cooled, ignited products.

Preliminary tests indicated that manganese chloride remained in the chlorination residue from which it could be recovered by water leaching. Because manganese chloride was thought to be a more valuable byproduct than iron chloride, an attempt was made to displace the iron in the slag by adding manganese ore while the ilmenite was being smelted. A slag having a lower iron content was produced in this manner and was subsequently used in the chlorination studies.

Specimens of commercial slag were furnished for chlorination tests by Quebec Iron and Titanium Corp. The slag had been produced primarily for sulfate-process pigment production and contained appreciable amounts of calcium, magnesium, silicon, and aluminum. Although accepted as an excellent material for sulfate-process pigment production the slag did not chlorinate well. The portions of the aluminum and silicon contents that are chlorinated appear either in the stack gas or in the intermediate condenser. Calcium and magnesium form liquid chlorides that cause operating problems.

Preliminary investigations were made in laboratory-scale equipment to determine carbon requirements and to study the effect of particle size and temperature on chlorination of a typical slag. The lowest practical reaction temperature was 480° C. Particles larger than 65 mesh did not chlorinate well. Subsequent tests were made using minus 200-mesh material to determine the most efficient reaction temperature and carbon requirement.

Ground slag and carbon black were briqueted to make a feed that could be handled without crumbling and that did not disintegrate to powder when chlorinated. For tests using reaction temperatures in the range of 605° to 763° C, best titanium recovery was 85 pct. Other major products were $FeCl_3$ and $MnCl_2$. Manganous chloride remained in the chlorination residue. Ferric chloride and titanium tetrachloride were produced as vapors and were effectively separated by condensing at different temperatures. A significant fraction of columbium was also chlorinated, and much of the $CbCl_5$ formed was recovered in the $FeCl_3$ product. No effort was made to recover a separate columbium product.

The theoretical amount of carbon required to react with the TiO_2 in 100 g of slag was 25 g, assuming that the reaction product was CO. Use of excess carbon increased the reaction rate but resulted in larger amounts of fine material remaining in the residue. For these tests, 35 g of carbon per 100 g of slag was found to give the best overall efficiency. Electric furnace slags containing 80 to 85 pct TiO_2 chlorinated readily to produce an acceptable commercial grade of $TiCl_4$. Best results were obtained with slag that had been ignited at 800° C. Based on earlier chlorination experience, it was assumed that carbon requirements are best determined experimentally for each process and feed material (*191*).

Vertical-Shaft Chlorinator

Preliminary laboratory tests indicated that investigations in larger scale equipment would be warranted. Accordingly, a 4-in-diam vertical-shaft chlorinator and condenser system was designed and fabricated. Figure 17 is a schematic diagram of this apparatus. The highest production rate attained in this equipment was 39 lb/h $TiCl_4$ per square foot of bed area. The chlorine efficiency, based on production of $TiCl_4$, was 74 pct, and the titanium efficiency was 73 pct. Results indicate that titanium slags produced by smelting of Idaho alluvial ilmenite can be chlorinated readily to produce an acceptable commercial grade of $TiCl_4$. Better chlorine and titanium efficiencies were attained on vacuum-cooled and water-quenched slags that were ignited than on similarly cooled slags that were not ignited.

Additional Slag Chlorination Tests

Studies of titaniferous slag chlorination were extended to cover continuous-feed reaction techniques and slags from a variety of starting materials (*162-163*). Moving-bed reactors of 4- and 36-in diam and a 6-in-diam fluidized-bed reactor were used. Slags tested contained, in percent, Ti, 41-60; Fe, 1.9-8.9; Si, 0.1-1.8; Al up to 9.1; Ca, up to 0.95; Mg, 0.1-5.0; Mn, 0.4-3.8; and Cb, up to 0.85. Samples of rutile concentrate were also tested for

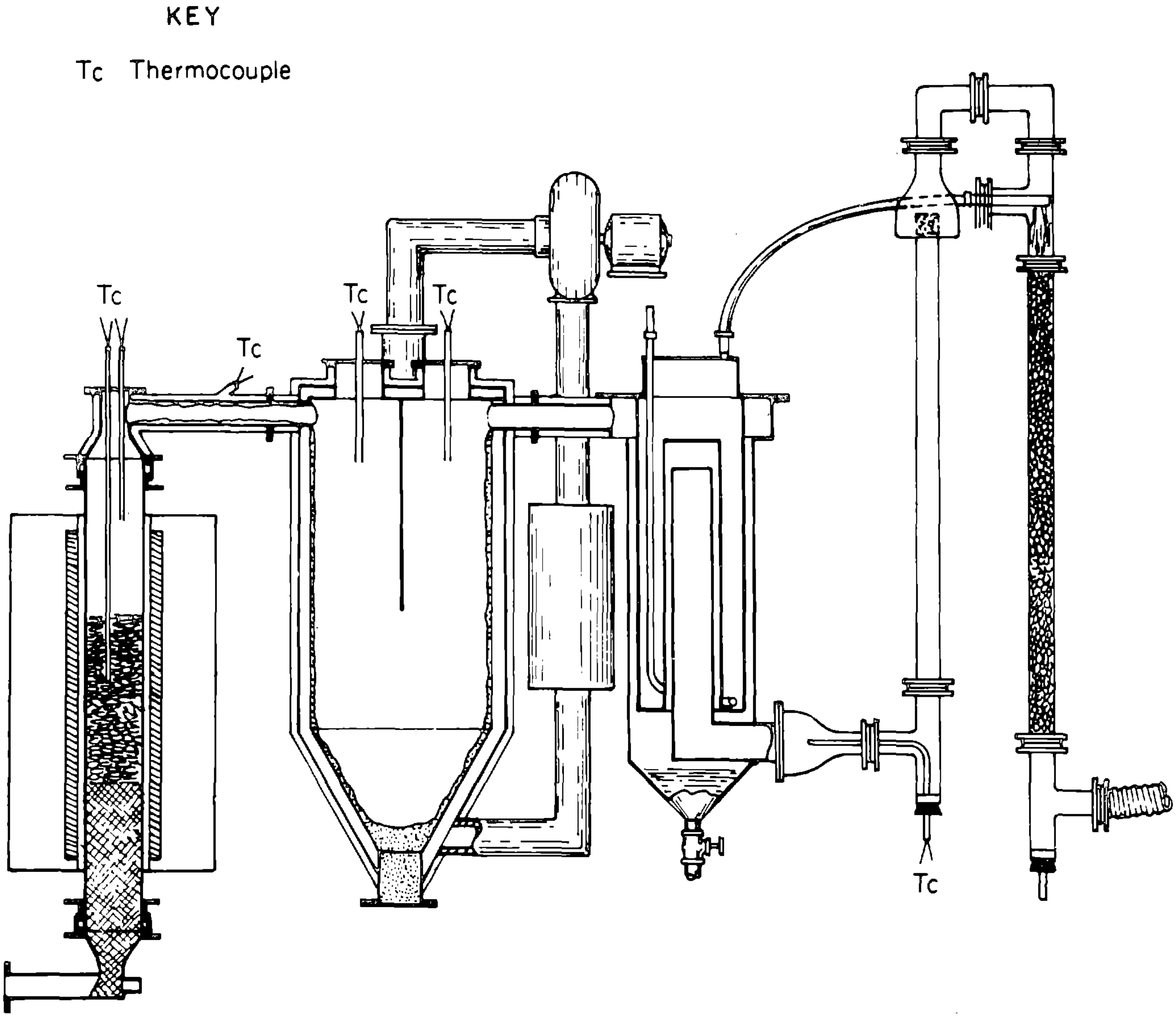

Figure 17.—Schematic diagram of slag chlorination unit.

comparison. Reaction temperatures of 500° to 1,000° C were used in the moving-bed tests; a higher temperature of 1,125° C was used in the fluidized-bed reactor because results of these tests were compared with results from tests using ilmenite, which requires a higher reaction temperature.

Many slag samples, as received, contained a significant fraction of plus 10-mesh material. These samples were chlorinated successfully in the 36-in-diam reactor without size reduction. Conditions were found for which chlorination efficiencies were 70 to 80 pct, comparable to those for rutile, for all samples except those containing more than 3 pct magnesium plus calcium. For the latter materials, solid or liquid magnesium and calcium chlorides formed that consolidated the reaction mass, and chlorination efficiency was significantly lower. In the fluidized-bed reactor test series, the use of an inert silica sand bed acted principally as a chlorine gas distributor and also served to dilute the impurity chlorides, which maintained the residue buildup at manageable levels.

Heats of reaction for some slag samples were not sufficient to maintain operating temperature, and supplementary heating was necessary. This was difficult to accomplish in the 36-in-diam reactor. Other test conditions could be maintained easily for tests with the 4- and 36-in-diam reactors, and data for these two units were in agreement on the relative amenability of the samples to chlorination.

Upgraded chlorination residue and synthetic rutile made from ilmenite slag were also chlorinated successfully *(50)*.

Tests demonstrated that the mineral synthesis technique can be applied to ilmenite concentrates from different sources to extract high-quality synthetic rutile. A three-step procedure that involves smelting of ilmenite to separate approximately 97 pct of the iron followed by synthesis and recovery of rutile in a low-iron slag fraction is required to prepare a crystalline product comparable with natural rutile in titanium content.

An ilmenite-to-carbon weight ratio of 6.2 or 7.2 can be used when smelting charges of Idaho or Tahawus, NY, ilmenite blended with lime at approximately 1,600° C to yield high-quality pig iron and titania-enriched slag.

Although titania slag can be oxidized at temperatures as low as 650° C, to convert the titanium-bearing phase to rutile, a higher temperature of approximately 1,500° C is recommended to synthesize crystals of a suitable size, 120 µm or more.

The use of a slag addition, anhydrous P_2O_5, ammonium-phosphate, or titanium pyrophosphate, is essential to obtain efficient rutile conversion and to facilitate recovery of the crystalline product from the glassy impurities. Of the three phosphorous-bearing additions tested, titanium pyrophosphate offers the most promise for use in large-scale operations.

Titanium dioxide content of synthetic rutile extracted from smelter slag was found to be dependent on treatment temperature as well as the proportion of flux added to slag. Rutile of 86 to 96 wt pct TiO_2 was recovered from oxidized slag charges fluxed with 9 wt pct TiO_2 at 1,000° to 1,500° C. Titania slag blended with additive with P_2O_5 content equivalent to 1 to 9 wt pct of the charge and heated to 1,430° C yielded synthetic rutile with TiO_2 contents of 86 to 93 wt pct.

In the liberation of rutile from the phosphate glass matrix, tests show that only 0.2 to 0.3 part sulfuric acid or 1 part phosphoric acid is required per part of ground slag.

Synthetic rutile-coke mixtures were reacted with chlorine in a fluid-bed reactor to convert more than 95 pct of the titanium in feedstock to $TiCl_4$.

CHLORINATION OF ILMENITE

Direct chlorination of ilmenite concentrates for the production of $TiCl_4$ has the obvious advantage of using a lower cost and more readily available raw material than either natural or synthetic rutile. It has the disadvantage of producing iron chlorides and chlorides of other impurity elements such as calcium, magnesium, and manganese as byproducts. Besides consuming chlorine, which must be recovered for recycle if the process is to be economical, impurity chlorides also introduce problems in operation of the fluidized-bed chlorinators and product recovery systems. Only DuPont Corporation has developed the technology required to handle large amounts of iron chlorides produced when ilmenite is used.

A generalized equation for chlorination of ilmenite may be written *(81)*:

$$FeTiO_3 + (x)Cl_2 + (y)C \rightarrow FeCl_3/FeCl_2 + CO/CO_2 + TiCl_4. \qquad (11)$$

The indefinite quantities of chlorine and carbon denoted by x and y result from the wide differences in ilmenite compositions and variance of $FeCl_3$-$FeCl_2$ and CO-CO_2 ratios with changes in processing conditions.

Chughtai *(28)* computed the equilibrium product distribution for the reaction of idealized ilmenite with chlorine and excess carbon at atmospheric pressure over the temperature range of 973 to 1,773 K and for weight ratios of $FeTiO_3$ to chlorine ranging from 0.4 to 1.0. The weight ratio of $FeTiO_3$ to chlorine is 0.61 for the stoichiometric production of ferric chloride and is 0.71 for the production of ferrous chloride. The results of the calculations over the range of temperature and ilmenite-chlorine ratio of most practical interest are shown in table 5.

The conclusions *(28)* were: (1) the excess carbon guarantees that the oxygen is completely removed from the iron and titanium except when the ilmenite-chlorine weight ratio exceeds 0.7, in which case titanium oxides are formed; (2) the ilmenite-chlorine weight ratios control the $FeCl_2$-$FeCl_3$ ratio; (3) temperature below about 1,173 K with ilmenite-chlorine weight ratios above about 0.7 lead to the formation of the high-boiling-temperature liquid $FeCl_2$; and (4) temperatures above 1,473 K with ilmenite-chlorine weight ratios above about 0.8 lead to the loss of titanium as solid TiC, while $TiCl_3$ with its attendant instability is an equilibrium product at the higher temperatures with ilmenite-chlorine weight ratios greater than 0.7. Thus the operating conditions for maximum yield of $TiCl_4$ and minimum excess chlorine are those of ilmenite-chlorine weight ratios from 0.6 to 0.7 and temperatures from 1,173 to 1,373 K.

The two significant differences between these calculations and the experimental fluidized coke-bed ilmenite chlorination results of Harris *(80-81)* are partially reconciled as follows. The much higher $FeCl_3$-$FeCl_2$ ratios averaging 40:1 found in the pilot-plant work are due in part to the presence of a cyclone separator in the product stream, which removes some of the liquid $FeCl_2$ before the analysis is made. Also, the average experimental CO_2-CO ratio of 1.7 is much higher than predicted, and is

Table 5.—High-temperature heterogeneous equilibrium compositions, mole fraction

Compound	[1]1,123 K	[1]1,223 K	[1]1,323 K	[1]1,423 K
ILMENITE-CHLORINE WEIGHT RATIO—0.60				
$TiCl_4$	0.171	0.169	0.166	0.164
$FeCl_3$	.140	.133	.114	.090
$FeCl_2$	.014	.030	.050	.073
Fe_2Cl_6	.008	.002	.001	(2)
Fe_2Cl_4	(2)	.001	.001	(2)
Cl_2	.019	.027	.036	.045
Cl	(2)	.001	.003	.007
C(s)	.151	.137	.132	.129
CO	.480	.496	.496	.492
CO_2	.017	.004	.001	(2)
ILMENITE-CHLORINE WEIGHT RATIO—0.65				
$TiCl_4$	0.174	0.173	0.171	0.169
$FeCl_3$	.094	.094	.085	.069
$FeCl_2$	.058	070	.083	.099
Fe_2Cl_6	.004	.001	(2)	(2)
Fe_2Cl_4	.007	.003	.001	.001
Cl_2	.001	.002	.007	.014
Cl	(2)	(2)	.001	.0004
C(s)	.157	.143	.139	.137
CO	.488	.510	.512	.507
CO_2	.017	.004	.001	(2)
ILMENITE-CHLORINE WEIGHT RATIO—0 70				
$TiCl_4$	0.176	0.174	0.173	0.172
$FeCl_3$	.020	.020	.020	.019
$FeCl_2$	.104	.133	.145	.150
$FeCl_2$ (liq)	.006	(2)	(2)	(2)
Fe_2Cl_4	.023	.011	.004	.002
Cl	(2)	(2)	(2)	.001
C(s)	.159	.143	.140	.138
CO	.494	.515	.517	.518
CO_2	.018	.004	.001	(2)

[1] To convert to degrees Celsius, subtract 273.2.

[2] Less than 0.0005.

attributed in part to the lower temperature of the analysis compared to the temperatures of the computations.

An isothermal plane from this system at 1,000° C is shown in figure 18 (*28, 82*) to illustrate the effect of varying ilmenite-chlorine feed ratios on the mole fractions of products and byproducts.

Domestic ilmenite concentrates differ considerably from the idealized $FeTiO_3$ formula and contain numerous impurities that affect processing. Impurities such as calcium, magnesium, and manganese cause processing difficulties because their chlorides have low vapor pressures and accumulate in the fluidized bed or in the cyclone and condensing systems. Vapor pressure curves for the products and common impurity chlorides are shown in figure 19. These curves illustrate why it is necessary to process at high temperatures and gas velocities to carry the impurity chlorides out of the fluidized bed. Chlorides of ferrous iron and some impurities may be present in the liquid state, indicating the need for rapid chilling of the vapors to form free-flowing powders rather than dense adherent accretions or gummy solid-liquid mixtures. Data (*82*) indicate that fractional condensation should allow separation of these chlorides into three groups: (1) the high-boiling-point chlorides of Ca, Mg, Mn, and Fe(II); (2) chlorides of Fe(III) and Al; and (3) the low-boiling-point $TiCl_4$ product, which contains small amounts of V and Si chlorides.

The Bureau first reported on the direct chlorination of ilmenite concentrates in 1955 as part of an investigation of the preparation and chlorination of titaniferous slags from Idaho ilmenites (*15, 178*). Ilmenite concentrate containing 41 pct TiO_2 and 35 pct Fe was mixed with 27 pct C and briqueted. After firing at 700° C, the briquets were chlorinated at 700° C for 6 h in the 4-in-ID fixed-bed chlorinator previously described in connection with rutile chlorination experiments. Chlorine efficiency was reported as 34 pct and titanium efficiency was 61 pct.

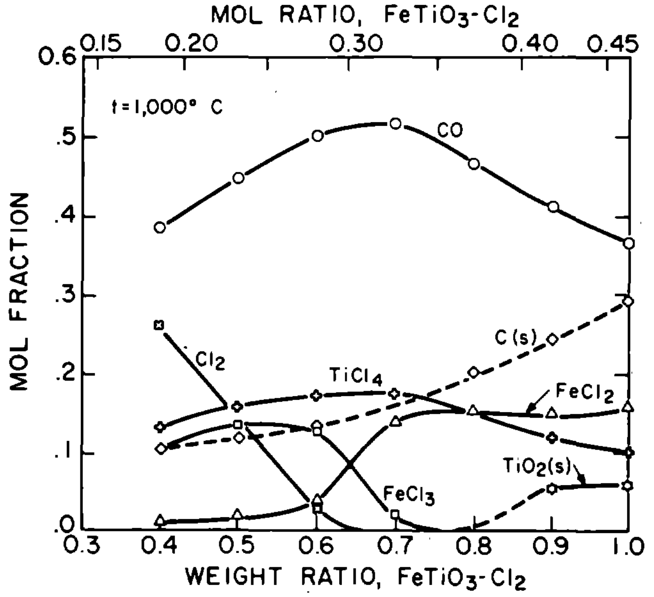

Figure 18.—Calculated mole-fraction of reactants and products at equilibria at 1,000° C in the C-Cl_2-$FeTiO_3$ system.

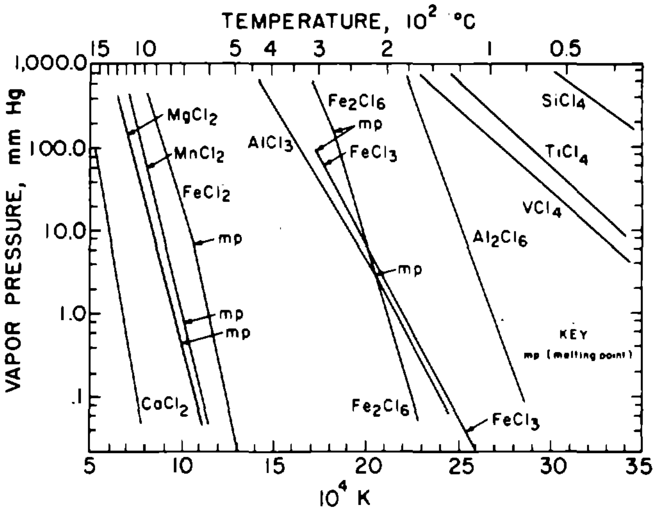

Figure 19.—Vapor pressure of chlorides.

Chlorination rate was about half that of the slags tested under the same conditions, and the authors warned that the production of 1.1 lb $FeCl_3$ for each pound of $TiCl_4$ poses a problem of consequence since chlorine consumption would be doubled and the disposal of large amounts of $FeCl_3$ would be difficult.

Research on direct chlorination of an Idaho ilmenite concentrate containing 27.9 wt pct Ti and 35.6 wt pct Fe was carried out at Boulder City (*160*) under a contract with the General Services Administration (GSA) to study the utilization of domestic ilmenite. The ilmenite used in these tests was a concentrate from an alluvial deposit in Valley County, ID (*102*), produced as a byproduct of monazite sand-dredging operations.

Chlorination took place in a 4-in-ID moving-bed chlorinator in which a screw feeder was used to feed ilmenite blended with 12 to 15 pct C into the top of the unit. A discharge port at the bottom of the chlorinator permitted intermittent removal of reacted material.

The solid impurities formed in the condensate when ilmenite is chlorinated may be as much as 50 pct by weight. Such a $TiCl_4$-$FeCl_3$ mixture is not fluid and cannot be handled by conventional condensing systems; therefore, either a trap for $FeCl_3$, or a special condensing system is necessary. The trap used in this work removed $FeCl_3$ from the gas stream by combining it with NaCl to form a low-melting eutectic (*161*). The following nonstoichiometric equation illustrates what occurs:

$$FeCl_3(gas) + NaCl(solid) \rightarrow \underset{(liquid)}{[FeCl_3 + NaCl]} \quad (12)$$

The composition of the melt is about 24 pct NaCl and 76 pct $FeCl_3$ by weight. After passing through the trap, the $TiCl_4$ is free of solid impurities and is condensed by cooling (*163*).

A weighed bed of quartz sand (99 pct SiO_2) was placed in the chlorinator to prevent clinkering in the bed due to preferential formation of iron chlorides. All attempts to start with an ilmenite bed resulted in a solid mass cemented with $FeCl_3$, which the chlorine gas could not penetrate.

Titanium extraction ranged from 82.2 to 82.5 pct and chlorine utilization was 91.2 to 93.3 pct for three runs. Analysis of the product $TiCl_4$ compared favorably with commercial-grade product.

Fluidized-Bed Chlorination of Ilmenite

Idaho ilmenite was chlorinated in a fluidized bed as part of a series of tests at Boulder City on fluidized bed chlorination of titaniferous slags and rutile concentrates (*163*). This was a continuation of the project sponsored by GSA to investigate the processing and utilization of domestic titanium ores.

The ilmenite concentrate used analyzed 27.8 pct Ti, 34.0 pct Fe, and 2.95 pct Mn. The 6-in-ID fluidized-bed chlorinator used an inert starting bed of minus 48-mesh silica sand to insure proper gas distribution when operating with small amounts of feed in the bed. Titanium extraction was 83.1 pct and chlorine utilization was 93.1 pct. No difficulties were encountered in chlorinator operation, but no attempt was made to separate the reaction products. Long-term tests were not made. It is likely that accumulations of $MnCl_2$ would probably cause the fluidized bed to become sticky during an extended run.

Coke-Bed Chlorination of Ilmenite

Use of coke as the major constituent of fluidized beds for the chlorination of ilmenite has advantages over other bed materials. It assures the availability of an excess of reductant and permits accurate control of the ilmenite-chlorine ratio and therefore of the $FeCl_3$-$FeCl_2$ ratio. The use of finely ground ilmenite feed and continuous monitoring of chlorine in the offgas is necessary to prevent overfeeding and loss of control of the $FeCl_3$-$FeCl_2$ ratio.

Initial Bureau of Mines fluidized coke-bed research (*81*) was conducted in a 1.8-in-ID Vycor reactor. Iron chlorides were collected as powders in two condensers maintained at 170° C, and these were followed by a salt-column filter to remove uncondensed $FeCl_3$. $TiCl_4$ was collected in a condenser cooled to −16° C by refrigerated brine.

Tests were conducted using ilmenite concentrates from Florida, New Jersey, New York, and Idaho containing 33.2 to 63.0 pct TiO_2 and with Ti-Fe ratios of 0.5 (Idaho) to 1.8 (Florida). Most of the tests reported were made with Florida ilmenite ground to 85 wt pct minus 100 mesh and with minus 35-mesh coke. The effect of chlorination temperature was investigated over the range 500° to 950° C. At 800° C and above, more than 98.7 wt pct of the ilmenite reacted. Results indicated that high efficiencies could be achieved at 750° C and above over a range of ilmenite-chlorine feed ratios. At a chlorine feed rate of 1.73 L/min and ilmenite feed rates of 3.3 to 4.6 g/min, there was little ilmenite carried over into the upper zone of the reactor or into the iron chlorides. At a reaction temperature of 950° C, considerable $FeCl_2$ was formed, as would be expected.

All ilmenite concentrates tested were efficiently chlorinated in the fluidized coke bed with recovery of satisfactory iron and titanium chloride products by fractional condensation. Only small amounts of soluble and insoluble materials accumulated in the coke bed, which remained free flowing during continued use.

Further fluidized coke bed ilmenite chlorination tests were conducted (*80*) using a reactor consisting of a 10.2-cm-diam quartz tube heated externally by electrical resistance heaters. Coke beds from 35.6 to 82.5 cm in depth were fluidized by 13 to 25 L/min of chlorine. Ilmenite concentrate powders were introduced at the bottom of the reactor, using the chlorine gas stream as a carrier. Operating temperatures were 950° to 1,150° C. More than 90 pct of the ilmenite reacted at optimum conditions and recovery of $TiCl_4$ ranged from 95 to 99 pct. A temperature-controlled cyclone was used to remove high-boiling-point chlorides such as $MnCl_2$, $MgCl_2$, and $FeCl_2$, and also collected fine, unreacted ilmenite and coke dust. Impure $TiCl_4$ and $FeCl_3$ were separated by collecting the iron chloride in a condenser controlled at 200° C. Titanium tetrachloride vapor was cleaned by passage through a salt-column filter followed by condensation in water-cooled and refrigerated condensers. Liquid $TiCl_4$ was purified further by well-known industrial methods to meet specifications for pigment grade chloride. Integrated tests were conducted in which chlorine produced by dechlorination of $FeCl_3$ with oxygen was recycled and used directly in a fluidized-bed chlorinator.

Results of tests in the 10.2-cm-diam reactor were similar to those in the 5.1-cm-diam reactor previously described (*81*), except that higher reaction temperatures were possible with a vitreous silica rather than Vycor reactor. Output of the larger reactor was approximately six times that of the smaller reactor for an area ratio increase of four, but higher reaction temperatures were used.

The $FeCl_3$ byproduct, with other chloride impurities, had a fairly low insoluble (ilmenite) content and was reacted with oxygen in another unit to make Fe_2O_3 and chlorine for recycling to the chlorinator. A manganese byproduct was made from the soluble portion of the cyclone dusts; the insoluble portion, mainly ilmenite and coke dusts, may be recycled to the process to increase recovery of $TiCl_4$.

A flowsheet for an ilmenite chlorination process based on these experiments is shown in figure 20 (*80*) and the equipment is illustrated in figure 21.

The 10.2-cm-diam fluidized-coke-bed chlorinator system just described was modified for further testing as described below and shown in figure 22 (*82*). The vitreous

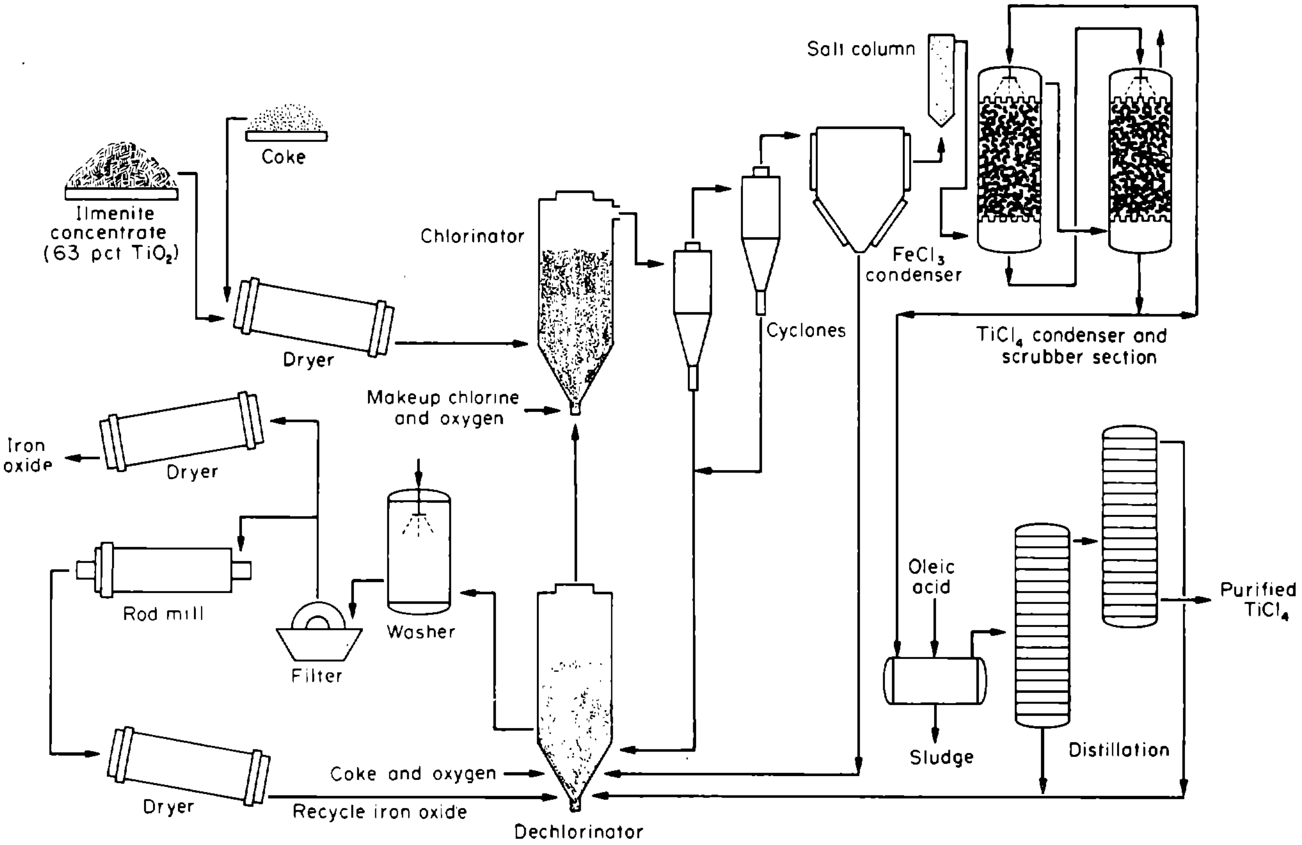

Figure 20.—Flowsheet of ilmenite chlorination process.

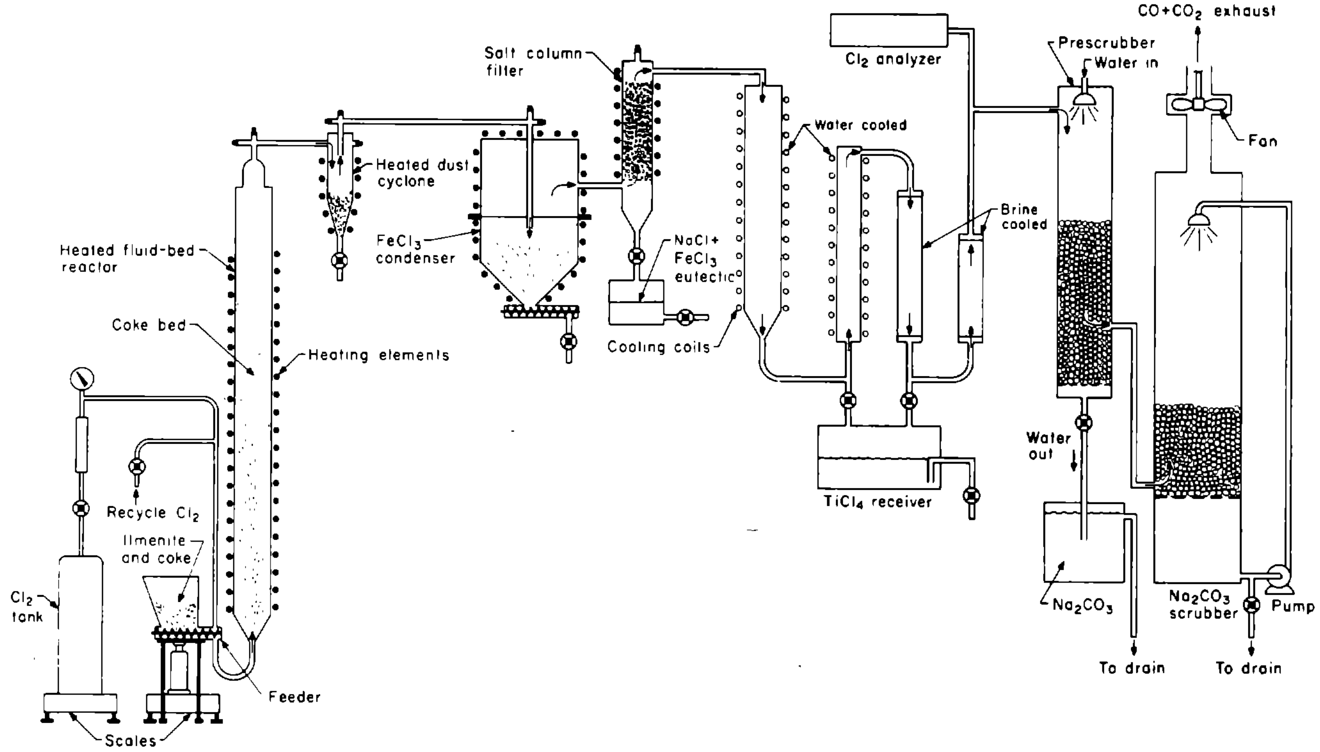

Figure 21.—Unit for chlorinating ilmenite in a fluidized bed.

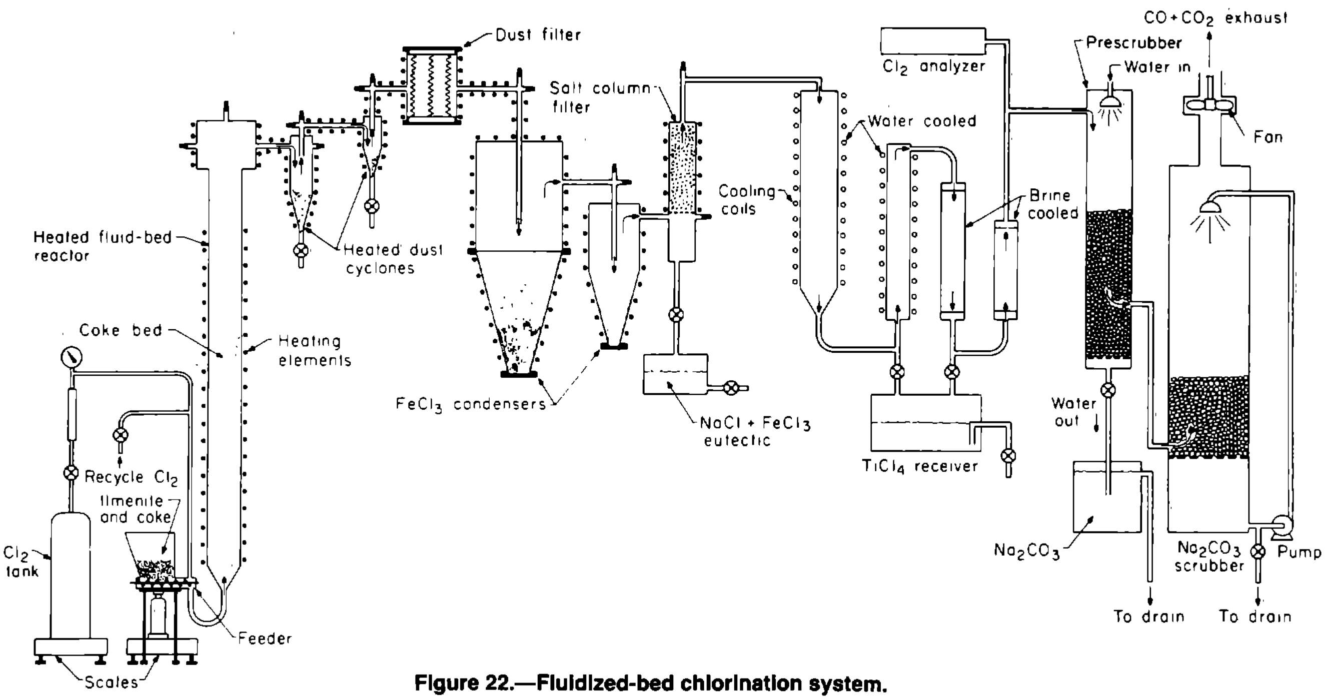

Figure 22.—Fluidized-bed chlorination system.

silica reactor was provided with a Fiberfrax-lined Inconel alloy top that was connected by a crossover tube to the first cyclone. Two cyclones and a fiberglass impingement dust filter were used between the reactor and the first iron chloride condenser to obtain a clean iron chloride byproduct. All of the components from the top of the reactor to the $TiCl_4$ condensers had uncoated, bare-metal inner surfaces and were externally heated and insulated to control fractional condensation. Primary $TiCl_4$ condensers were constructed of Pyrex Double-Tough glass pipe and were cooled by exterior tube coils and hollow plates inside the pipe. The final two $TiCl_4$ condensers were shell-cooled glass units. Brine at approximately 10° C was used as coolant in the $TiCl_4$ condensers.

The same ilmenites from Florida and New York were chlorinated in this modified system at 1,050° C using chlorine flow rates of 18 to 20 L/min. Concentrates were tested both as received (minus 35 mesh) and ground to minus 100 mesh. Results at close to optimum conditions are given in table 6.

The percent of ore reacted was lower with the Florida ilmenite concentrate because of the higher feed rate and the fact that it is less reactive than the New York concentrate. Some unreacted ilmenite enriched in TiO_2 accumulated in the bed material and would have been recovered as $TiCl_4$ in a continuous operation. Most of the ilmenite- and coke-dust carryover was collected in the first cyclone and the impingement filters along with most of the less volatile chlorides. Clean iron chloride byproducts were collected that contained only very low amounts of ilmenite and coke dust. Iron chloride containing less than 1 pct ilmenite dust is necessary to permit dechlorination to yield iron oxide with a low enough titanium content to be acceptable for use in steelmaking.

Table 6.—Results of chlorination tests of ilmenite concentrates

Ore feed rate, g/min	Ore size, mesh	Length of test, h	Ore reacted, pct	$TiCl_4$ recovery, pct	Cyclone ore,[1] pct
NEW YORK ILMENITE					
27.4	−35	10	95.6	96.0	1.8
32.4	−100	4	96.0	96.5	1.8
FLORIDA ILMENITE					
38.2	−35	10	91.2	95.0	0.4
31.6	−100	14	95.5	99.2	3.2

[1] Ore caught in cyclone, unreacted.

The ratio of ore to coke in the bed was allowed to reach higher levels than in previous tests by not making coke additions in the final hours of the tests, to determine if operating problems would result. No difficulties with fluidization of the bed were encountered in any of the tests with either type of ore. The minor amounts of soluble chlorides found in the bed after tests using the New York concentrate were rich in $CaCl_2$ and $MgCl_2$, but $MnCl_2$ was also present in the beds from tests using the Florida concentrate.

Design and construction of a 10-in-diam integrated chlorinator-dechlorinator system was halted in 1976 when the project at the Albany (OR) Research Center was terminated. Bench-scale investigation of fluidized-bed chlorination of ilmenite was reinstituted at Albany in late 1981. The primary objective was to make fresh $FeCl_3$ for dechlorination tests and secondarily to examine the effects of temperature and other operating variables on the chlorination operation.

CHLORINATION OF REDUCTION PRODUCTS

Chlorination of natural or synthetic rutile, ilmenite, or slags in the presence of carbon requires relatively high temperatures (800°-1,200° C). However, if the titanium content is first reduced to TiO, TiC, TiN, TiCN, or combinations of these compounds, chlorination becomes highly exothermic and can proceed at temperatures below 500° C. For this reason, the prevailing practice for production of $TiCl_4$ prior to about 1960 was to convert the titanium in rutile to the cyanonitride by high-temperature reduction in an electronic-arc furnace followed by chlorination of the cyanonitride. The disadvantages of this process are the high energy requirements of the arc-smelting process, the use of high-grade rutile concentrates in the charge, and the presence of several percent of $SiCl_4$ in the finished product.

In 1949, Knickerbocker (*111*) reported on work done at the Rolla (MO) Research Center on preparation of titanium chloride and oxide from titanium mattes. Mixtures of ilmenite or rutile with pyrite and coke were smelted at 1,550° C to produce a titanium sulfide containing matte and metallic iron. Chlorination of the mattes at 200° to 220° C produced a yellow, crystalline solid containing 17 to 21 pct Ti, 4 to 6 pct S, and 67 to 75 pct Cl_2. This product was reportedly identified as a mixture of $TiCl_4$ and titanium sulpho-octochloride ($TiCl_4 \cdot SCl_4$). Recovery of titanium in the chlorination product was 60 pct and refining of this product to pure $TiCl_4$ was difficult.

Gorski (*72*) reported, in 1951, on investigations at Rolla on the chlorination of carbon-reduced rutile. A sample of rutile concentrates from Hot Spring County, AR, containing 76.19 pct TiO_2, 5.65 pct Fe_2O_3, 4.18 pct SiO_2, and 2.88 pct Al_2O_3 was used for this investigation. Mixtures of minus 100-mesh rutile and petroleum coke were sintered at 1,050° to 1,400° C to form a reduction product identified as a mixture of titanium suboxides and minor amounts of TiC. The reduction product was then ground to minus 100 mesh, mixed with 30 pct of its weight of minus 100-mesh petroleum coke, and chlorinated.

Several series of runs were made to study the effect of varying the amount of petroleum coke and reaction temperature on the reduction of rutile and subsequent chlorination of the reduced product. More than 95 pct of the titanium could be recovered consistently when the rutile was reduced at 1,200° to 1,400° C with an excess of coke and then chlorinated at 500° C. When the reduction temperature was less than 1,050° C, the titanium recovery was lowered considerably. Further experimental work showed that the reduced rutile could be chlorinated at temperatures as low as 136° to 144° C, approximately the boiling point of $TiCl_4$, with a recovery of 84.6 pct of the titanium in the rutile.

The chief advantage of this method of preparing $TiCl_4$ is the low chlorination temperature of 200° to 500° C. Also, the product is substantially free from silicon compounds, thus making the purification simpler than the purification of commercial, technical grade material that usually contains several percent of $SiCl_4$.

DECHLORINATION OF IRON CHLORIDES

Domestic ilmenite is a low-grade source for titanium, which is both plentiful and less expensive than rutile. However, processing and waste disposal problems currently limit ilmenite's use in the manufacture of $TiCl_4$. In the direct chlorination of ilmenite in a fluidized-bed reactor, the high iron content of ilmenite results in large amounts of iron chloride waste products. These large amounts of iron chlorides, principally $FeCl_3$, represent a major loss of chlorine in the process and pose a costly and increasingly difficult waste disposal problem.

There is extensive literature describing efforts over the last several decades to develop a commercially viable process which would recover Cl_2 from $FeCl_3$ and generate a benign iron compound. The most promising route seems to be by reacting $FeCl_3$ with oxygen at high temperatures as described by the reaction

$$2FeCl_3 + 3/2O_2 \rightarrow Fe_2O_3 + 3Cl_2. \qquad (13)$$

A number of processes and reactor designs have been proposed to effect this reaction including moving-bed reactors (*46*), fluidized-bed reactors (*44, 74, 175-176, 182*), flame-type reactors (*144*), and tubular, vapor-phase reactors (*60, 107*).

When the Bureau of Mines began investigating the dechlorination of $FeCl_3$ in 1970, the fluidized-bed reactor was chosen for further study. Tests with a 5.1-cm-ID fluidized-bed reactor by Henderson (*87*) indicated high conversions of $FeCl_3$ were possible between 500° and 600° C. These tests also pointed out the catalytic activity of NaCl in the Fe_2O_3 bed at levels of 1 pct or less. The catalytic activity presumably involves the formation of $NaFeCl_4$ (*1*) on the surface of the Fe_2O_3 particles that make up the bed. Based on these results, further studies were planned and a 16.5-cm-ID fluidized-bed reactor system was constructed and is shown in figure 23 (*156*).

Early tests identified three operating problems: carryover of unreacted $FeCl_3$, plugging of the $FeCl_3$ inlet line, and a reduction in surface area of the Fe_2O_3 bed material. A feed was then tested which consisted of 75 pct $FeCl_3$ and 25 pct Fe_2O_3. This mixture reduced plugging in the $FeCl_3$ feed-inlet line and provided sufficient fresh Fe_2O_3 in the bed to prevent the surface area reduction and deactivation of the bed material. Further tests with this reactor and feed mixture identified the bulk density of the $FeCl_3$ feed as a factor affecting both the conversion of $FeCl_3$ and the formation of wall accretions in the reactor. Low-density $FeCl_3$ (0.8 g/cm^3) yielded higher conversions than high-density $FeCl_3$ (2.0 g/cm^3). No explanation was found for this effect.

A final test was made incorporating all the experience gained to that time. The reactor was operated for 30 h at 500° C with a feed of 75 pct $FeCl_3$ (1.2 g/cm^3) and 25 pct Fe_2O_3. Conversion of $FeCl_3$ was approximately 99 pct, offgas produced was 57 pct Cl_2, and only occasional plugging occurred in the feed lines (*82*).

Work on $FeCl_3$ dechlorination was discontinued in 1975. At that point, three major problems areas had been identified as standing in the way of a commercial process:

1. Providing sufficient heat to sustain the reaction with a commercial-scale reactor;
2. The buildup of wall accretions inside the reactor due to $MgCl_2$, $CaCl_2$, and $MnCl_2$ accumulation;
3. Further improvements were needed in $FeCl_3$ feeder operations (*82*).

Several industrial-sector research programs continued after this point, resulting in some notable patents. E.I. du Pont de Nemours & Co. continued working on a fluidized-bed process. A pilot plant was operated at feed rates as high as 3,520 kg/h $FeCl_3$, utilizing NaCl as a catalyst, and recirculating fresh Fe_2O_3 to the reactor. Process heat was provided by burning a low-hydrogen carbonaceous fuel (*175*).

Mitsubishi Metal Corporation's efforts during this time were directed towards a synthetic rutile process in which the iron in ilmenite was selectively chlorinated and, without being condensed, was reacted with oxygen in a tubular reactor. A 1-mt/d artificial rutile pilot plant was operated for up to 30 days utilizing this approach (*60, 107*).

Bureau of Mines research on chlorine recovery from $FeCl_3$ resumed in fiscal year 1981. Two types of reactors are being tested with the goal of overcoming the three previously identified problem areas of providing heat to the reactor, preventing wall accretions, and reliably feeding $FeCl_3$ to the reactor.

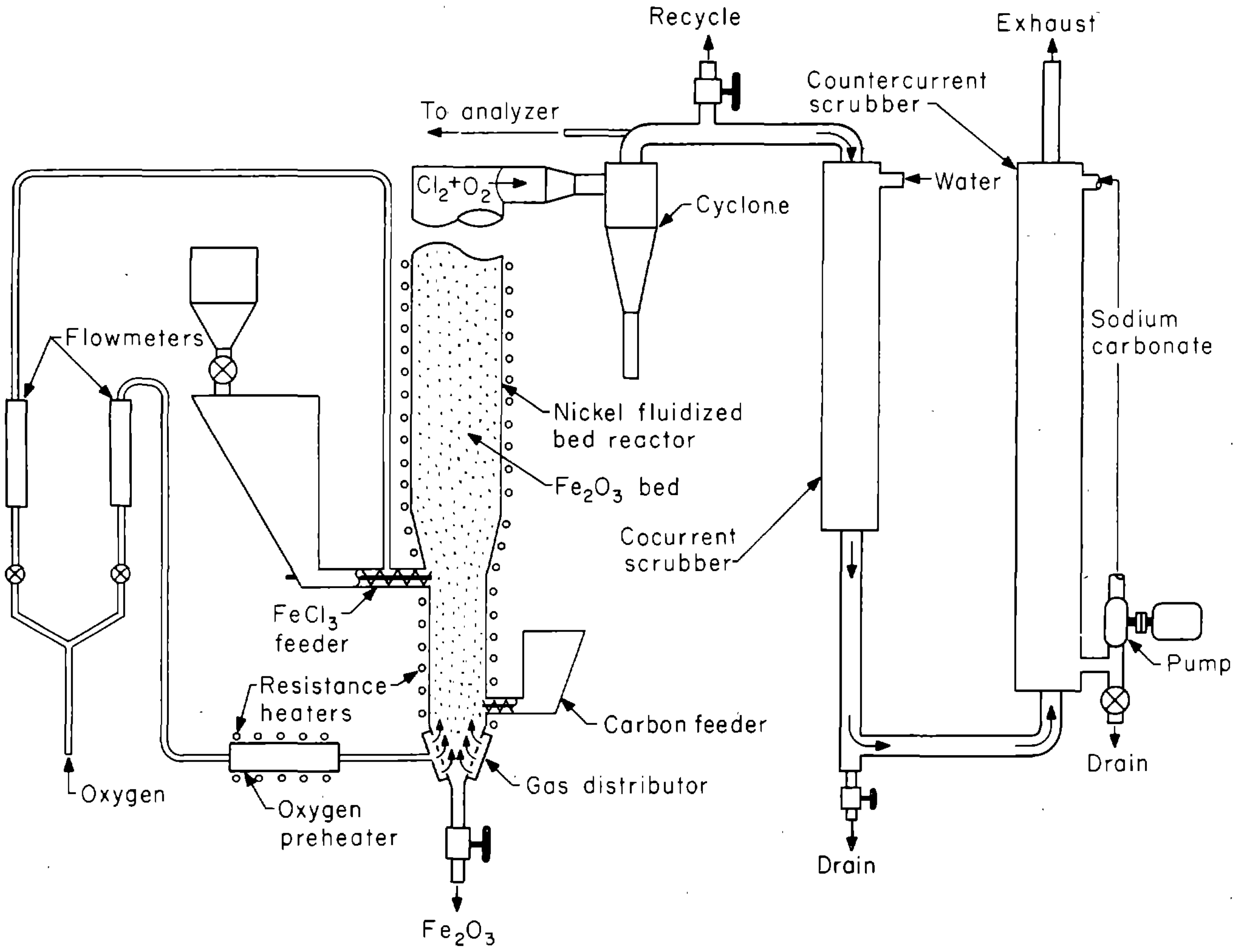

Figure 23.—Fluidized-bed reactor for conversion of $FeCl_3$ to Fe_2O_3 and Cl_2.

A 16.5-cm-ID fluidized-bed reactor was built and tested. A reliable feeding system has been devised in which pelletized $FeCl_3$ is entrained in a high-velocity stream of oxygen and injected to the bottom of the reactor (*150-151*). Pellets of various compositions have been made and successfully fed to the reactor in this way. As a means of heating the reactor, the burning of metallic iron in the bed was examined. This offers several advantages over the use of carbonaceous fuels. Iron ignites reliably, does not dilute the Cl_2 product gas, and continuously produces fresh Fe_2O_3 in the reactor. Preliminary economic analyses indicate that prereduced iron pellets, such as those produced for steelmaking, would be competitive with coke as a fuel. Various ratios of $FeCl_3$, Fe_2O_3, Fe, NaCl, and O_2 are being examined for their effect on conversion and the buildup of wall accretions in the reactor.

The second approach being tested reacts $FeCl_3$ and O_2 in a vertical, tubular quartz reactor. $FeCl_3$ pellets are fed to a boiler containing a molten mixture of $FeCl_3$ and NaCl at 500° to 600° C. Ferric chloride vaporizes as a dimer, Fe_2Cl_6, which depolymerizes on further heating to $FeCl_3$. This mixture of $Fe_2Cl_6(g)$, along with a small amount of $Cl_2(g)$, added to suppress decomposition to $FeCl_2$ is delivered to the top of a vertical, tubular quartz reactor where it is mixed with a stream of $O_2(g)$. The gases mix and react as they travel cocurrently downward through the reactor. Finely divided $Fe_2O_3(s)$ produced by the reaction is entrained in the flowing gases, providing fresh catalyst for the reaction.

As the reaction products leave the reactor, $Fe_2O_3(s)$ and any unreacted $FeCl_3$ are separated from the gases, which then are analyzed for Cl_2 content. In this case, the heat necessary to maintain the reaction temperature of 650° to 800° C is provided through the boiler in the form of heats of fusion and vaporization of $FeCl_3$ and the heat of the dissociation reaction. The relatively low vapor pressures of the contaminant chlorides ($MgCl_2$, $CaCl_2$, $MnCl_2$) should allow them to accumulate in the boiler where they can be bled off for treatment rather than in the reactor where their presence as a liquid contributes to hard, dense wall accretions.

The effects of operating variables and of additives such as $AlCl_3$ on reactor efficiency and Fe_2O_3 product properties are being investigated.

PURIFICATION OF TITANIUM TETRACHLORIDE

Titanium tetrachloride as obtained from the condensing system of a commercial rutile chlorination operation is not suitable for metal production. Depending on the raw materials, equipment, and procedures used, the impurities vary considerably from one plant to another and even between production lots from a single plant. The impurities may be dissolved or consist of suspended solids. Common dissolved impurities may include (1) gases such as chlorine, phosgene, carbonyl sulfide, and hydrochloric acid; (2) chlorides, normally liquids, such as carbon tetrachloride and several sulfur chlorides; and (3) any number of metal chlorides among which chlorides of silicon, vanadium, and iron are almost always present. Solid contaminants of almost any kind may be present; these are often very finely divided, even colloidal or jellylike. Common solids are carbon, silica, titanium dioxide or basic titanium oxychlorides, ferric chloride, and various other metal oxides. Solid contaminants can be removed by settling and decantation. Dissolved impurities with boiling points above and below the boiling point of $TiCl_4$ can be separated by distillation. Some metal chlorides, dissolved gases, and possibly some organic impurities require a chemical means for their removal.

Subsequent to issuance of the Kroll patent and Bureau publications on $TiCl_4$ reduction research, a large number of chemical purification agents were proposed. When the Bureau initiated research on $TiCl_4$ purification, very little information on purification methods had been published. Barton (*16*) mentioned the use of copper, mercury, or sodium amalgam to remove chlorine from freshly prepared $TiCl_4$. Pamfilov and Standel (*157*) heated distilled tetrachloride over gold, silver, mercury, copper, or bronze to remove the yellow color. Pechukas (*159*) suggested the use of H_2S for removal of iron, vanadium, molybdenum, and possibly other unidentified impurities; SO_2 for removal of excess H_2S; and subsequent distillation to produce a colorless $TiCl_4$.

Commercial $TiCl_4$ ordinarily has a reddish yellow to yellow color. Pure $TiCl_4$ is a colorless liquid. Its physical properties are listed in table 7 along with those of $SiCl_4$, its most similar impurity.

Table 7.—Physical properties of $TiCl_4$ and $SiCl_4$

	$TiCl_4$	$SiCl_4$
Molecular weight	189.73	169.89
Density at 20° C . . . g/cm³	1.723	1.486
Do . . . lb/gal	14.37	12.39
Do . . . lb/ft³	107.7	92.8
Specific heat, (Btu/lb)/°F:		
Gas	0.129	0.132
Liquid	0.188	0.191
Latent heat of vaporization at boiling point and 1 atm . . . Btu/lb	79.2	72.7
Trouton's constant	20.4	20.8
Boiling point at 1 atm . . . °C	136	56.8
Viscosity at 20° C . . . cP	0.8	0.5

Laboratory Investigations (*195*)

Methods for precise analysis of $TiCl_4$ were not available when the Bureau's research was started. The predominant analytical method used was flame spectrography, and the procedure became increasingly refined as the work progressed. For rapid evaluation of purification efficiency, it was fortunate that color was an excellent indication of purity except for $SiCl_4$ content, which could be precisely determined by distillation concentration followed by standard gravimetric analysis.

Raw Materials

Commercial $TiCl_4$ purchased from several manufacturers was used in the purification research. Analysis of five lots of commercial grade $TiCl_4$ from each of two suppliers is shown in table 8.

Table 8.—Chemical analyses of commercial grade $TiCl_4$ from sources A and B, grams per liter

Fe	V	S	Si	Free Cl_2	Non-volatile residue	Spectrographic trace elements
			SOURCE A			
0.03	1.9	0.15	0.26	2.00	1.7	Cu, Al, Pb, Mg, Mn, Ca, Cr, Sn
.04	1.9	.04	.40	1.90	1.75	Cu, Al, Pb, Mg, Mn, Ca, Cr
.03	1.7	.03	.25	1.98	3.4	Cu, Al, Pb, Mg, Mn, Ca, Ni
.04	1.2	.05	.25	1.02	5.4	Cu, Al, Pb, Mg, Mn, Ca, Cr
.04	1.1	.03	.25	1.30	5.9	Cu, Al, Mg, Mn, Ca
			SOURCE B			
0.05	1.8	0.06	0.27	2.97	1.70	Cu, Al, Mg, Mn, Ca, Fe, Sn, Cb
.04	1.9	.04	.40	1.90	1.76	Cu, Al, Mg, Mn, Ca, Fe, Pb, Cr
.03	1.7	.03	.25	1.98	3.40	Cu, Al, Mg, Mn, Ca, Fe, Pb, Ni
.04	1.1	.03	.25	1.30	5.90	Cu, Al, Mg, Mn, Ca, Fe
.03	95	.04	.15	3.55	4.20	Cu, Fe, Sn, Mo

Distillation

A number of small-scale laboratory distillations served to define the factors involved in the distillation of commercial $TiCl_4$. These tests showed that although $SiCl_4$ could be removed efficiently by distillation, separation of vanadium by distillation did not appear possible. It was of interest that the yellow color was not due entirely to vanadium compounds or products of hydrolysis, as the colorless distillate also contained vanadium.

A distillation test was run on about 300 mL of crude $TiCl_4$ with a laboratory glass-bead rectifying column. No attempt was made to promote efficient rectifying conditions and the column operated only with the reflux effect of the heat loss. A thermometer indicated the temperature of the vapor at the top of the column. The product was divided into two fractions by changing the receiver when the temperature at the top of the column rose from the boiling point of $SiCl_4$ (about 53° C) to the boiling point of $TiCl_4$ (about 131° C). Results showed that all of the $SiCl_4$ was separated in a fraction that contained 2 wt pct of the original charge and analyzed only 5 pct $TiCl_4$. It was evident that the $SiCl_4$ was readily separated by distillation, but the production of a colorless product was much more difficult.

Treatment With Hydrogen Sulfide

As distillation did not afford a practical method of producing a vanadium-free, colorless product, it was necessary to resort to other treatments.

The use of H_2S for the removal of iron, vanadium, molybdenum, and possibly other unidentified impurities, and the production of colorless $TiCl_4$ upon subsequent distillation, had been suggested by previous investigators (*159*). A number of tests showed that the vanadium could be removed at room temperature, that subsequent distillation was necessary to produce a colorless product, and that a crystalline precipitate formed that frequently plugged the inlet tube. Analysis showed the complete removal of vanadium.

Treatment With Copper

A series of tests with copper showed the relationship between the amount of copper powder, the temperature, and the time necessary to produce a colorless tetrachloride. In these tests, the copper powder was held in suspension by vigorous stirring, and the color was noted after the stirring was stopped and the copper powder had settled out.

The time of treatment required was reduced by heating, and about 1.5 pct copper powder was the minimum that would produce a colorless product. The powder used was prepared in the laboratory by reducing finely ground cuprous oxide with hydrogen. Spectroscopic tests showed that there was no pickup of copper by the tetrachloride undergoing treatment. Tests on samples of copper powder from commercial sources showed that absorption of oxygen by the copper would diminish or destroy its decolorizing effectiveness.

The copper powder turned black almost immediately when added to $TiCl_4$ and formed a hard cake when allowed to settle out after stirring was stopped. This cake contained about 75 pct of its weight in recoverable $TiCl_4$, which could be driven out by heating. The copper powder apparently reacted with the tetrachloride, as considerable heat was evolved when carefully purified tetrachloride was added to copper powder.

Treatment With Other Agents

A number of other agents were found to be effective for decolorizing commercial tetrachloride when added before distillation. These included oleic acid and other fatty acids and their salts and esters, such as occur in natural oils. Certain amines and napthenic acids and their salts and esters were also effective. Many other substances probably possess the ability to decolorize $TiCl_4$ in this same manner. The amount of these agents required to produce a colorless product varied somewhat, but generally was less than 1 to 1.5 pct. A series of tests demonstrated that addition of about 0.15 pct oleic acid was sufficient.

Distillation was necessary to separate colorless vanadium-free $TiCl_4$ from these reagents, which were slightly soluble and formed an intensely colored solution in the tetrachloride.

Pilot-Plant Investigations (*61, 195, 214*)

Equipment

The main objective of the pilot-plant operations was to produce purified $TiCl_4$ for the metal production program. Results of laboratory tests showed that both chemical treatment and distillation were necessary to produce reduction-grade $TiCl_4$ from commercially available tetrachloride, and therefore purification was accomplished in two stages. The chemical treatment stage was designed to allow use of copper powder, H_2S, or oleic acid, and the distillation stage was designed primarily to separate $SiCl_4$.

Chemical Reactor Vessel

The chemical treater was a closed mild steel vessel, with a capacity of about 112 gal. A high-speed stirrer was inserted through a flange port on the top of the vessel. Three electric immersion heaters were mounted in vertical convection tubes at the sides of the tank. The liquid contents were discharged by air pressure through a vertical line that passed through a packing gland. This arrangement permitted vertical adjustment to accommodate varying residue levels in the bottom of the vessel. A 6-in flanged cleanout port was located at the bottom of the tank to remove the reaction residues.

Distillation Unit

A batch distillation procedure was chosen over continuous rectification for separation of $SiCl_4$ from $TiCl_4$ because less equipment was required and because it was a simpler operation and less sensitive to maladjustment. The major equipment items were the still boiler, the rectifying column, the condenser, and separate receiving tanks for $SiCl_4$, intermediate fraction, and purified $TiCl_4$.

The still boiler was constructed of 1/4-in steel plate and held approximately 65 gal. In the initial design, heating was by three 3,000-W immersion heaters. Later, the boiler was encased in a rectangular oven of insulating brick, and heating was provided by an electrial resistance grid a few inches below the bottom of the boiler. The oven and boiler were mounted on a platform scale so that the weight of material in the boiler could be determined at any time.

The rectifying column was made up of sections of 4-in steel pipe joined by standard flanges. The column was packed with rings made from 22-ga black sheet iron. The height of the column was varied from 8 ft at the start of the pilot-plant operation to 11 ft, and finally to 14 ft in an attempt to improve $SiCl_4$ separation.

The condenser was constructed of 1/4-in seamless steel tubing arranged in a hexagonal bundle of 19 tubes, 20 in long. Vapor condensed on the outside of the tubes. The product stream passed to a combined reflux splitter and hydrometer box where the stream was divided between reflux returning to the top of the column and product to the receivers. Control of the streams was provided by rotameter flowmeters.

A line of the pilot-plant equipment, indicating material flow, is shown in figure 24.

Operating Procedure

Chemical Treatment

The addition agents were added to the chemical reactor vessel with the high-speed stirrer in operation. When copper powder was used, it was added in 2-lb increments approximately every 15 min. Addition of the first 2-lb increment when the tetrachloride was still cold aided in surpressing the emission of free chlorine and resulted in less obnoxious fume during later additions when the material was hot. The total amount of copper powder added was usually 2 wt pct of the crude $TiCl_4$. For H_2S treatment, the crude $TiCl_4$ charge was added, the heaters and stirrer were started, and the charge was heated to 200° F. During the 2 h required to heat the charge, 0.5 lb of H_2S was added. After the charge was heated, the rate of reaction was increased so that during the next 3 h, a quantity of H_2S varying from 1.5 to 3.5 lb was added. Determination of the total addition of either copper or H_2S was based on the distillation of a small sample from the treater. If a colorless distillate was obtained, the treatment was considered complete.

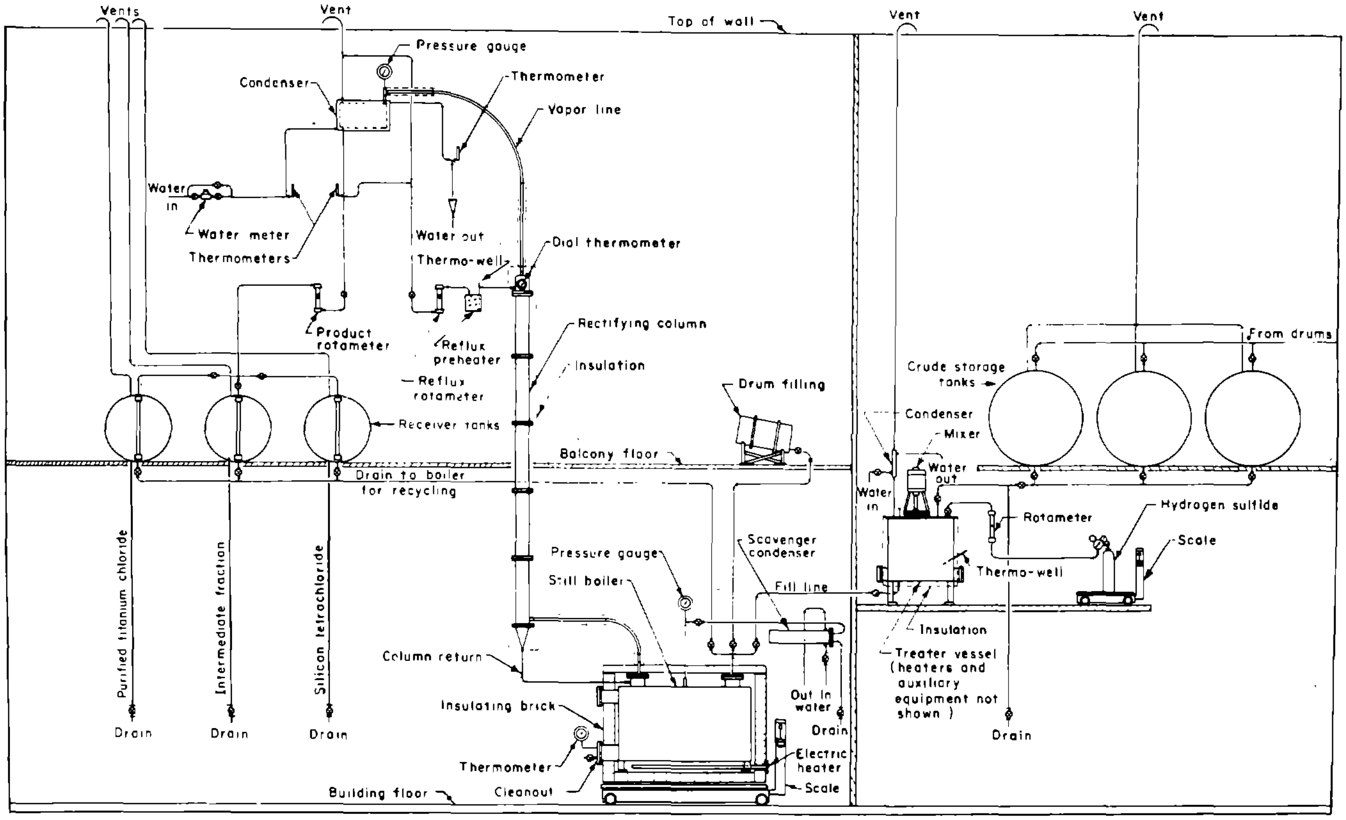

Figure 24.—Line diagram of equipment used for purifying titanium tetrachloride.

Spent copper sludge was usually removed from the treater after 100 to 150 lb of copper had been added. The sludge was collected in a drum, which was sealed, connected to a condenser system, and heated in an oven at 300° F for 48 h and at 550° F for 5 to 6 days. The distillate was returned to the chemical reactor vessel for reprocessing. The remaining copper residue contained 60 to 80 pct Cu. The balance was mainly $TiCl_4$ and, presumably, oxygen.

When oleic acid was used for the chemical treatment, the chemical reactor vessel was bypassed, and the crude $TiCl_4$ was added directly to the still boiler with about 0.15 wt pct of oleic acid.

Distillation

Treated tetrachloride was transferred from the reactor vessel to the still boiler by applying air pressure to the reactor vessel. At the start of a distillation cycle, the valves were set so that all of the condensate returned to the column as reflux. This condition was maintained until a steady state was reached. The control valves were then set so that part of the condensate stream flowed to the $SiCl_4$ receiver. The reflux ratio was adjusted to a value of about 1:1. Distillation was continued in this manner until there was an abrupt change in temperature at the column head, whereupon the condensate stream was switched to the intermediate receiver, and the reflux ratio was adjusted to about 4:1. The intermediate fraction was collected with an accompanying rise in column-head temperature, until a constant temperature of 274° to 276° F was reached, and for approximately 20 min thereafter. The condensate stream was then switched to the pure $TiCl_4$ receiver, and the reflux ratio was reduced to about 1:1. Distillation was continued until about 100 lb of liquid remained in the boiler.

The intermediate fraction could be recycled to the boiler either as bleed-in or as a complete charge if the total silicon content of the charge, expressed as $SiCl_4$, was not more than 40 g/L. When the silicon content was higher than this, use of a higher reflux ratio was necessary during distillation of the first two fractions, and the percentage of the charge taken off in the intermediate fraction had to be increased.

Complex silicon compounds accumulated in the intermediate fraction, which eventually became so high in silicon that it could no longer be distilled, and another treatment was required. One of the most effective procedures was to vaporize the liquid mixture and heat the vapor to at least 850° C. The complex silicon compounds were decomposed by this treatment into $SiCl_4$ and various other substances markedly less volatile than $TiCl_4$. The silicon-containing impurities could be removed by fractional distillation.

Dissolved hydroxychlorides and solid matter from the chemical reactor vessel accumulated slowly in the still boiler. Usual practice was to bake the still dry after treating about 4,000 lb of titanium chloride. The vapor line to the rectifying column was closed and the distillate was condensed in a special condenser. The baking out, using less energy than used for normal distillation, took about 24 h. A dry fluffy residue was removed from the still. The weight of the dry material ranged from 5 to 12 lb. The condensate was returned to the crude tetrachloride stream.

Effect of Reflux Ratios (*195*)

The most important operating variable for distillation was the reflux ratio expressed as the ratio of the weight of the reflux stream to the weight of the product stream. Theoretical studies by Rose and Long (*179*) on batch distillation have shown that the size of the intermediate fraction decreases as the reflux ratio is increased. Increasing the reflux ratio also decreases the useful output of the system for any given rate of vaporization, however. Vaporization rate was limited by the vapor velocity at which the column flooded or spray was carried over into the product. Rate of vaporization was, of course, proportional to the heat input.

The effect of the reflux ratio is shown by a series of six special runs made with the height of the rectifying column at 8 ft. Data for the runs are summarized in table 9. The initial composition of the charge for each run was approximately 20 wt pct $SiCl_4$. Although it was desired to have the initial composition and weight of the boiler charge the same in all runs, some variation occurred. However, this was not sufficient to be significant in the final results. During the course of the run, samples were taken from the product stream at the time the level or weight of the contents of the boiler was noted. The composition of the samples was determined from their specific gravities as obtained by a Westphal balance.

Table 9.—Summary of data from the special runs

Run	Av reflux ratio indicated	Av heat input, kW	$TiCl_4$ in initial charge, pct	Intermediate fraction		Av holdup of initial charge pct
				Size, pct	Elapsed time to end, min[1]	
1	0.87	5.57	79.3	16.9	223	(2)
2	2.28	5.51	79.3	12.3	257	(2)
3	5.11	4.57	79.1	7.2	355	(2)
4	1.02	5.48	80.3	19.9	253	1.44
5	2.20	5.37	78.8	12.7	333	.69
6	5.03	4.84	79.2	6.6	455	.66

[1] Taken from start of distillation to end of condensation of intermediate fraction.

[2] Indeterminate.

The rate of distillation was taken as the sum of the flowmeter readings in the product and reflux lines and was held approximately the same for all runs by adjustment of the heat input. Some variation occurred from run to run. Run 1 served as the operating pattern for the other runs, except that in subsequent runs, the heat input was raised markedly during the period when the intermediate fraction was distilling. This was to compensate for the rather large and sudden demand for the heat that was absorbed by the column as its temperature increased from the boiling point of $SiCl_4$ to that of $TiCl_4$. After this demand had been satisfied, the heat input was held constant until the termination of the run.

Runs 1, 2, and 3 were started after the column was operating at equilibrium conditions and total reflux. Efforts were made to adjust the reflux ratio to that desired as quickly as possible after starting the run by diverting product to the receiver. Runs 4, 5, and 6 were similarly started from equilibrium conditions, but with the valves set for the desired reflux ratio by returning the product to the boiler through a special line. In this case, the run was started by switching the product stream from the boiler return line to the receiver. All initial charges contained enough $SiCl_4$ so that complete separation took place, and the overhead vapor was pure $SiCl_4$ when equilibrium was established and the distillation was started. Considerable care was taken to hold the indicated reflux ratio constant by flow-ratio adjustment during a run. The actual value of the reflux ratio, as determined by a heat balance, was not important in this series of test runs as long as the indicated reflux ratios were relatively constant and reproducible.

Data from the six runs are plotted in figure 25, in which the weight percent of the original charge that was distilled is plotted on the abscissas and the weight percent of the $TiCl_4$ in the product is plotted on the ordinates. These are typical batch distillation curves. Integration of the area beneath the curves provided a convenient check of the accuracy of the curve position because the area should be equal to the composition of the original charge according to the basic theory of batch distillation (*34*).

This criterion revealed that the curves for runs 1 and 2 are badly out of position, whereas curves for the remaining runs are accurately located. This displacement was due to some error in measuring the boiler contents; therefore, it is assumed that the shapes of the curves are essentially correct and can be used to indicate the degree of sharpness of separation obtained by the different reflux ratios.

The method of measuring the boiler contents was changed from sight-glass gage readings to actual net changes in boiler weight between runs 3 and 4, when the entire boiler assembly was placed on platform scales. The break in the curves was very sharp after the $SiCl_4$ fraction had distilled but was relatively more gradual at the end of the intermediate fraction. The reflux ratio had virtually no effect on the $SiCl_4$ break and moderate effect on the intermediate fraction break, making it sharper with higher reflux ratios.

The size of the intermediate fraction decreased markedly as the reflux ratio increased. Similarly, the time necessary for removal of the $SiCl_4$ increased as the reflux ratio increased. A greater length of time was required for the $SiCl_4$ removal when distillation was started from equilibrium at the required reflux ratio than when the start was from equilibrium at total reflux.

The knowledge gained from the special runs was used in setting procedures for the operation of the still on a continuous basis. A virtually pure $SiCl_4$ fraction was removed that did not require any further treatment for recovery of valuable $TiCl_4$. The fractionation points were determined by the temperature of the vapors at the top of the column, as shown by an abrupt temperature rise at the end of the $SiCl_4$ fraction, which continued to a constant value at the end of the intermediate fraction. The slow break at the end of the intermediate fraction indicated that care must be taken not to cut off the intermediate fraction before the last of the $SiCl_4$ was eliminated from the product. Complete elimination of the last traces of $SiCl_4$ would make the intermediate fraction unduly large; hence, a maximum limit of 0.015 pct $SiCl_4$ was set for the continuous production campaigns, which theoretically would yield a metal containing 0.01 pct Si after reduction. At the start of a run, a steady-state condition at total reflux removed the $SiCl_4$ in the shortest time.

The curves of figure 25 show how the reflux ratio can be varied to give the greatest production rate for a given heat input. To obtain pure $SiCl_4$, low reflux ratios were used during the period the $SiCl_4$ fraction was coming off. When the temperature rise at the end of the $SiCl_4$ fraction indicated that the intermediate fraction was beginning to come over, the reflux ratio was raised to between 4:1 and 5:1 to sharpen the separation and decrease the burden of

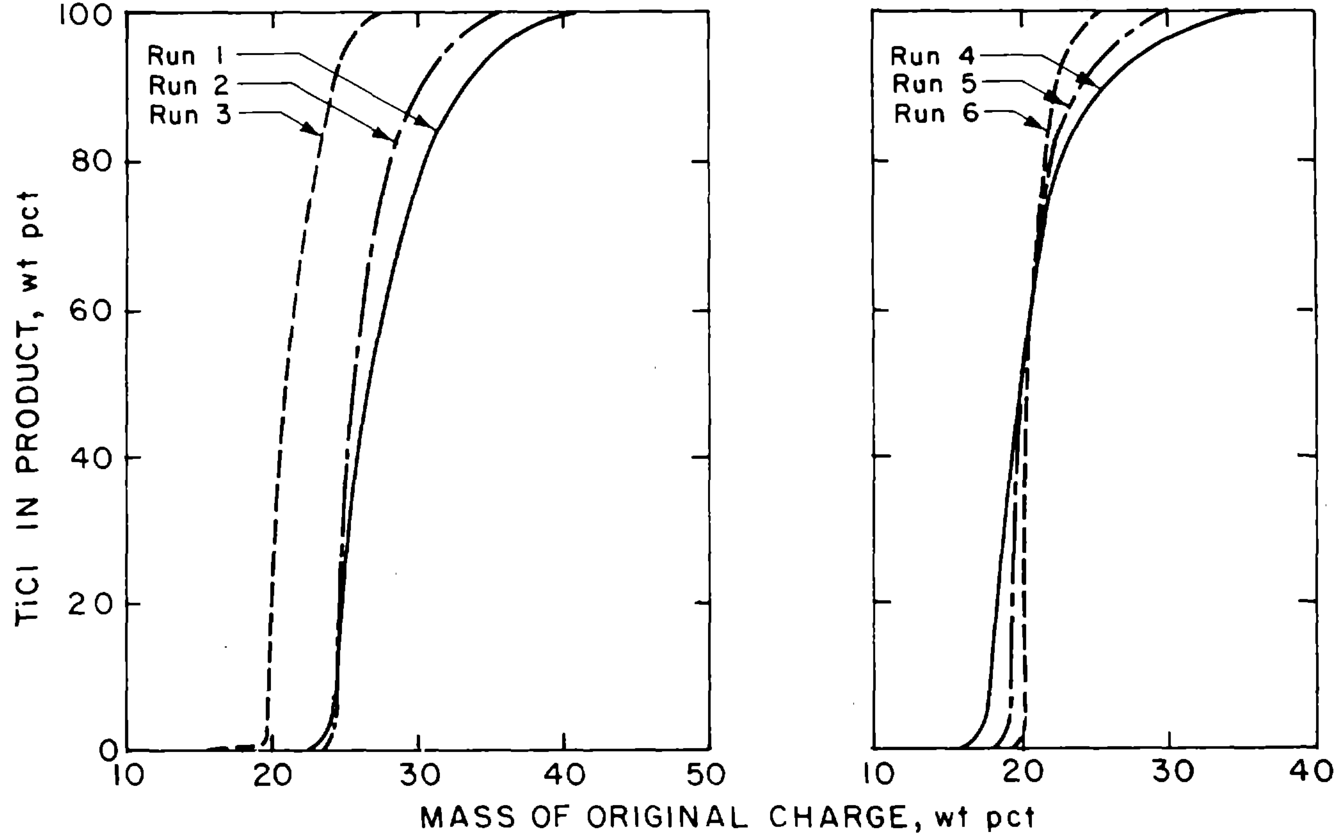

Figure 25.—Batch distillation curves for special runs.

rerunning the intermediate fraction for the recovery of $TiCl_4$. After the intermediate fraction had passed out of the system, the pure $TiCl_4$ was distilled rapidly by reducing the reflux ratio to a low value or even by cutting the reflux off entirely when no higher boiling point components were present in the boiler.

Production Operation

Material Balance

Table 10 lists a material balance for two refining campaigns. Each campaign was on a separate lot of crude $TiCl_4$. One lot was treated by the copper powder method and the other by the oleic acid method. Recovery of the $SiCl_4$ was low, as it was difficult to condense this volatile substance completely without refrigeration. The material balance for campaign 1 shows that only about 60 pct of the $SiCl_4$ originally present was recovered. A part of this was lost in the copper treater due to the inefficiency of the condenser on the vent line. The $SiCl_4$ was of no value to the process, so this loss was not significant to the investigation. Recovery was generally satisfactory, and it was reasonable to expect better recoveries could be attained on a routine production basis.

Table 10.—Materials balance on two campaigns

	Campaign 1		Campaign 2	
	lb	pct	lb	pct
Material in: Crude $TiCl_4$	22,404	100.0	7,244	100.0
Material out:				
Purified $TiCl_4$	21,273	95.0	7,030	97.1
$SiCl_4$ fraction[1]	270	1.2	0	0
Left in system[2]	145	.6	16	.2
Loss and unaccountable	716	3.2	198	2.7
Total	22,404	100.0	7,244	100.0

[1] No $SiCl_4$ was collected from the lot 2 tetrachloride; the small amount present was collected with the intermediate fraction.

[2] This includes the last intermediate fraction at the end of the campaign.

NOTE.—1.94 lb Cu powder per 100 lb $TiCl_4$ charged (campaign 1); 145 lb oleic acid per 100 lb crude $TiCl_4$ charged (campaign 2).

The upper limit of the capacity of the column was never reached. Flooding or significant pressure drop was never observed, even with full power of about 9 kW and total reflux. This indicated that a higher production rate could be attained by installing larger heaters. The results indicate that it would be dangerous to the color and possibly the purity of the product to attempt to gain a higher production rate by reducing the reflux stream.

Heat Balance

Table 11 shows a heat balance for one complete batch or still charge. It indicates that about 85 pct of the heat output was in the condenser discharge water. This table shows that 497 Btu was required to produce a pound of product, starting from the cold still with a crude material containing very small amounts of silicon tetrachloride and intermediate fractions.

Demonstration Plant (*13*)

Raw Materials

A $TiCl_4$ purification plant was constructed as an integral part of a demonstration plant capable of

Table 11.—Illustrative heat balance on one complete batch
(70° F condenser inlet water)

	Temp, °F	Wt, lb	Btu		pct of total
			Per lb	Total	
Heat input:					
Charge in still	90	757	3.6	2,730	0.9
Condenser water	71	36,550	NAp	0	0
Electric power	NAp	NAp	NAp	299,000	99.1
Total	NAp	NAp	NAp	301,730	100.0
Heat output:					
Charge in still	278	105	38.9	4,080	1.4
Condenser water	78	36,550	7.0	255,850	84.8
$SiCl_4$ fraction	77	7	1.1	Neg	<.1
Intermediate fraction	82	38	2.0	Neg	<.1
$TiCl_4$ product	79	607	1.5	910	<.1
Unaccounted for[1]	NAp	NAp	NAp	40,890	13.5
Total	NAp	Nap	NAp	301,730	100.0

NAp Not applicable.
Neg Negligible.
[1] Includes heat necessary to heat boiler shell and column.

producing about 1,500 lb/d of titanium metal. Crude $TiCl_4$ was purchased from commercial producers.

Equipment and Material Flow

$TiCl_4$ from the commercial producers was stored in three horizontal, round steel tanks with a capacity of 10,000 gal each. $TiCl_4$ was unloaded from rail tank cars through a 1-in-diam line by use of dry compressed air pressure at about 28 lbf/in^2(ga). The only pump necessary was for lifting the tetrachloride from the storage tanks to the sulfider at the beginning of purification. Other transfers of liquids requiring small heads or lifts were generally made with dry compressed air.

Purification Equipment

A diagrammatic flow sheet of the purification facility is shown in figure 26.

The sulfiding pot was a steel cylindrical vessel 48 in. in diam by 48 in. in length with a capacity of 420 gal, or about 6,000 lb, of $TiCl_4$. It had dished heads and was mounted horizontally. The bottom half was surrounded by a rectangular sheet-steel skirt, which enclosed four tubular, pinhole propane-gas burners, each running nearly the length of the pot. A propeller-type agitator was directly connected to a 2-hp, 1,150-r/min motor. The pot was emptied by gravity to the fractionation still.

The fractionation still was the same size and similar to the sulfider and was equipped with the same type of heating apparatus. In the bottom part of one end was a 10-in flanged, circular cleanout opening, normally closed with a blind flange. At the bottom of the other end was a 2-in flanged drain connection facing toward the pot still. At the top, in the center, was a 4-in flanged opening flanked on both sides by 2-in flanged openings. Mounted over the 4-in opening was a 4-in-diam fractionating column 23-ft high, which was filled with 3/8-in carbon steel Raschig rings. The column was heated by a resistance-wire heating element wrapped around the column for a distance of 20 ft.

The pot still was 72 in. in diam by 28 in high with a flat bottom and domed top. Like the sulfider and fractionation still, it was equipped with propane gas burners. On one side at the bottom was a standard flanged, 10-in cleanout normally covered with a blind flange having a 1-in valved drain at the bottom. On the opposite side, extending horizontally from near the top, was a 2-in flanged connection through which feed entered by gravity from the fractionation still. Directly in the center of the pot-still dome was a 4-in flanged opening that was surmounted by a foam and entrainment trap. The trap also acted as a very small dephlegmator or partial condenser, yielding enough condensate to wash any spray and solid entrainment back into the pot still.

The sulfiding pot and the two stills were insulated on their upper exposed surfaces with a 2-in layer of Micalite and the fractionating column, partial condenser, and pot-still vapor line were insulated with a 2-in layer of rock wool.

$TiCl_4$ was pumped from crude storage to the sulfiding pot. From there it proceeded by gravity successively through the fractionation still and the pot still. The vapors from the pot still passed up to the condensers, and the condensate passed by gravity into storage tanks.

The condensers were of the surface-condensing type, constructed of 11-ga sheet steel. Each consisted of a 1-in-wide parallelepiped for the vapor chamber surrounded by a water compartment 0.5 to 1.5 in larger all around.

A partial condenser, 26 in long by 15 in high, received vapor from the fractionating column. The main condenser, which followed the partial condenser, was 51 in long by 15 in high. Vapor entered the vapor compartment at the top, and condensate left the opposite end through a 1-in standard iron-pipe nipple. The condenser for the pot still was of similar construction but slightly larger, 63 in long by 18 in high. Condensate from the pot still condenser flowed down through a cooler that consisted of a piece of 1-in pipe shaped like a hairpin, which was water jacketed and had a total length of 120 in.

The steam reflux condenser on the partial condenser and a similar one on the sulfiding-pot vent line consisted of a 24-in length of vertically held 0.75-in pipe surrounded by an 18-in jacket of 1.5-in pipe.

Operating Procedures and Results

The operating procedures and techniques for purifying $TiCl_4$ were based largely on the experience gained in operating the pilot plant. Normal purification took place in three steps: (1) treatment with H_2S in the sulfiding pot, (2) fractionation in the fractionation still, and (3) final distillation in the pot still.

Sulfiding Operation

The amount of H_2S required was determined by a laboratory test on a sample from each carload as it was received. In the plant operation, a normal batch of 300 gal, or about 4,400 lb, was pumped from crude storage to the sulfiding pot. The batch was heated to between 90° and 100° C, and the H_2S was added at a rate of 1 lb/h while the charge was agitated vigorously. During this operation, the sulfiding pot was vented to the main vent chamber through the cooled pipe condenser, and an undetermined quantity of low-boiling components was removed. Most batches required between 4 and 8 lb of H_2S, and occasional batches required up to 10 lb. Precipitates formed were chiefly vanadium and iron compounds and added their bulk to the nonvolatile residues originally present in the crude tetrachloride. These residues were kept in suspension quite easily by the agitator and transferred to the fractionating still. The sulfiding pot required cleaning only once in 2 yr of operation.

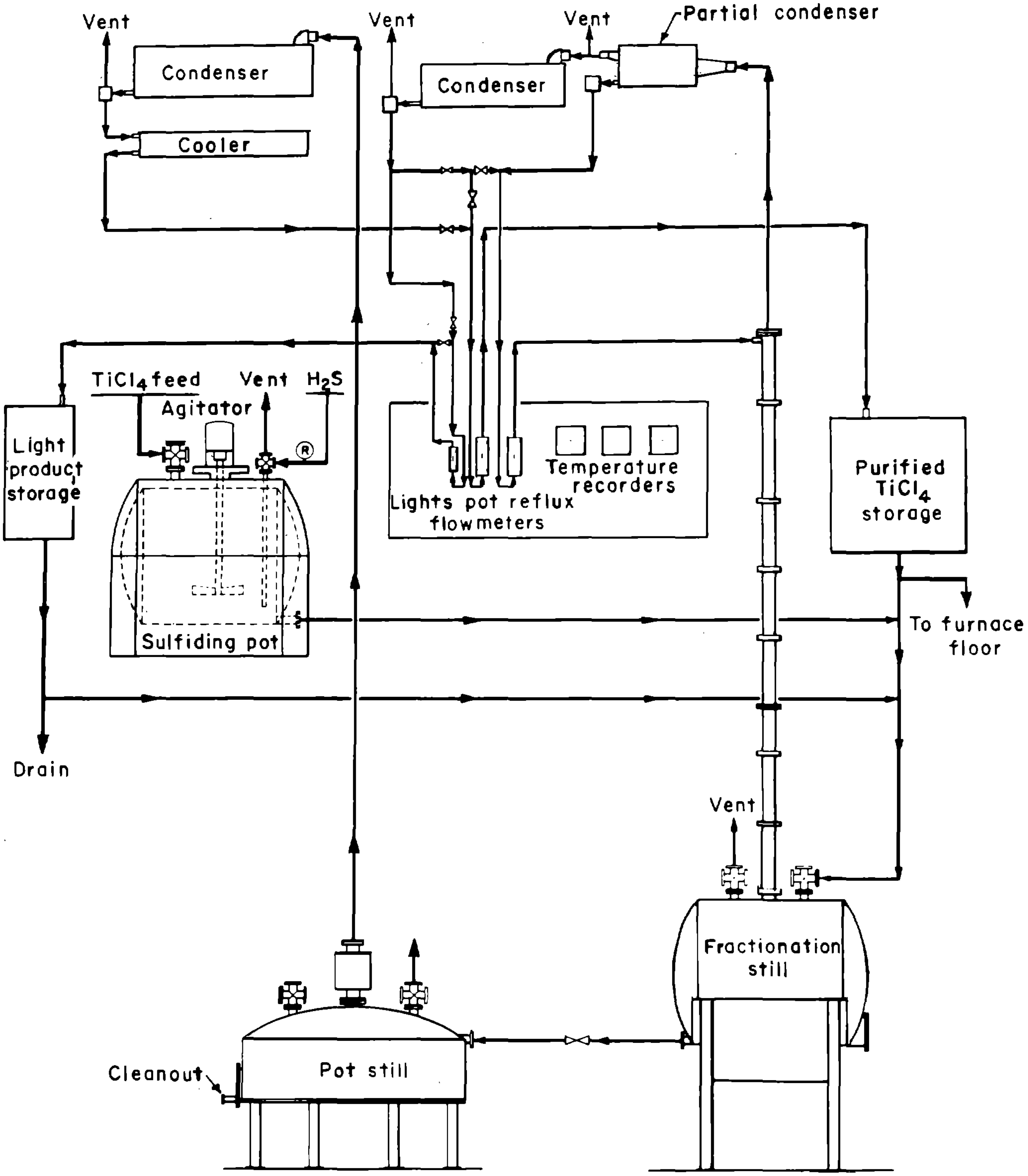

Figure 26.—Diagrammatic flowsheet of $TiCl_4$ purification.

After slightly more than the theoretical H_2S requirement had been added, the charge was allowed to flow by gravity to the fractionation still.

Fractionation

Fractionation was divided into two steps; the first was to bring the apparatus to equilibrium by a period of total reflux, and the second was the removal of a 150-lb fraction while the column was under partial reflux. Experience showed that 150 lb included all of the low-temperature $SiCl_4$ that could be removed efficiently and economically.

The partial condenser was started with about 2 gal of distilled water in the outer water jacket, which filled it about halfway. The two strip heaters attached to the sides were turned on, and in a short time, the water in the jacket was boiling. Meanwhile, cooling water was started through the main condenser, and heat was turned on the spirally wound resistance wire on the rectification column, which compensated for radiation through the insulation. The burners under the fractionating still were then turned on. As soon as the condensate appeared at the flowmeter from the partial condenser, the strip heaters on the partial condenser and the column resistance heater were turned off. The hot vapors from the fractionation still then maintained the heat in the system. Normal operating temperature of the fractionation still was approximately 136° C at a pressure varying from 1 to 1.5 $\mathrm{lbf/in^2}$(ga). The temperature at the top of the column varied from 132° to 134° C.

A period of total reflux was maintained for about 1.5 h, except for a light drip of condensate that came out of the main condenser and was allowed to flow to one of the two light-product storage tanks. This drip consisted of the very lightweight fractions with boiling points lower than 98° C, the temperature of the partial condenser.

At the end of the 1.5-h period, the distilled water was drained away from the partial condenser, and all gases went to the main condenser. The valve in the line to the second light-product storage tank was opened, and the valve in the line to the first light-product storage tank was closed. Thus, the very light products taken off during total reflux were kept separate from the second light or intermediate fraction. The first light product collected was small in quantity and usually contained at least 25 pct $SiCl_4$. In early operations, this material was discarded; later it was returned to crude storage, and finally, no distinction was made between the first and second light product recovered. In all cases, the second condensate and the combined condensate, when made, were returned to the succeeding batch in the fractionation still. Discarding the first distillate was the most positive way of removing silicon from the system. Recycling did not cause a buildup of $SiCl_4$, as might be expected, because its low boiling point of 58° C caused a large portion of it to be vented out of the system.

After equilibrium had been reached, the period of partial reflux was begun. Reflux ratios as low as 1:1 and as high as 4:1 were used, and the higher ratio was preferred. This ratio was maintained by manual adjustment of the valves on the line from the main condenser to the reflux flowmeter and the lights flowmeter.

During this part of the operation, the heat input to the fractionation still was regulated to maintain the column temperature at 136° C, slightly higher than the temperature used during the total reflux stage of the operation. Approximately 5 h were required to remove 150 lb of lights, which signified the completion of the partial reflux operation. The burners under the fractionation still were than turned off, and the processed batch was transferred by gravity to the pot still.

Distillation

Heat was applied to the pot still just as soon as transfer of the batch from the fractionation still was completed. This operation consisted simply of distilling over the pure $TiCl_4$ at 135° C and atmospheric pressure. The distillation rate was usually around 700 lb/h, and the entire operation in the pot still required between 6 and 8 h.

Approximately 1 in of liquid was usually left in the pot still at the end of a run. This was to prevent damage to the still from overheating and to cut down on the carryover of solids as mist. Nonvolatile residues were allowed to accumulate in the pot, and these were removed through the cleanout once a week. A bake period of about 14 h at 135° C was necessary to dry out the residue before removal. The residue amounted to about 2 pct of the total amount of $TiCl_4$ processed, or about 600 lb per week, and consisted largely of sulfur, sulfides and chlorides of titanium, iron, and vanadium and titanium hydrates. Typical analyses of pot-still sludge residues are shown in table 12.

Table 12.—Analyses of pot-still sludge, percent

	A	B
Al	ND	0.38
Cl	39.46	18.9
Fe	5.70	3.0
Mn	ND	.04
S	16.51	20.8
Si	.61	.43
Ti	36.6	ND
V	.72	.5

ND Not determined

Purified $TiCl_4$ was condensed, cooled, and conducted to the pure tetrachloride storage tanks where it was available for charging, by gravity flow, to the reactor feed tanks. Typical purified $TiCl_4$ contained 0.03 to 0.04 g/L Fe, <0.10 g/L V, 0.01 to 0.08 g/L S, <0.10 g/L Si, and <0.10 to 0.15 g/L of free Cl.

CHAPTER 3.—REDUCTION TO METAL

EARLY BUREAU OF MINES RESEARCH

In the spring of 1938, a meager research program to survey posible methods for the preparation of titanium metal that might be adapted to commercial production was initiated at the Bureau station in Tucson, AZ.

At that time, metallic titanium, produced either by the sodium reduction or hydride process, was available in limited quantities. However, neither process appeared well suited to large-scale production, for consistent production of high-quality product. The sodium reduction process required a high-pressure, high-temperature reaction in a steel bomb, which made it difficult to adapt the techniques to more than a few pounds per batch. The hydride process required high-cost reagents and depended on reduction of the oxide, which made it extremely difficult to obtain ductile metal because of the presence of residual oxygen. Thus, at the start of the Bureau's research program on titanium, no method was in use that appeared suited to large-scale production.

Early progress of the work was hampered both by a complete lack of experience on the part of the researchers and by inadequate facilities and funds necessary for critical evaluation of methods and techniques. The investigators had not the slightest conception of the extreme precautions necessary to prevent atmospheric contamination of metallic titanium at high temperatures. The analytical equipment and techniques available to the investigators were primitive by later standards, and in most instances, the degree of contamination of the reaction products was evaluated by appearance and by change in weight.

Perhaps it was better that the early investigators did not recognize the limits of their knowledge of the properties of titanium and the inadequacy of their equipment. Otherwise, it would have been established that the research was hopelessly handicapped, and the investigation would never have been started. In the work at Tucson, nonmetallic reducing agents such as carbon and hydrogen, as well as metallic agents such as aluminum, magnesium, and sodium, were tested. Decomposition in electric discharges and in electrolytic reductions was also tested. In the light of later developments, flaws in the basic theories, as well as in techniques, became obvious; but this was pioneering work, and with each failure, a little knowledge of the requirements for metal production was obtained.

A detailed description of the many early experiments conducted in the Bureau laboratories is not the purpose of this report, as many of the experiments were complete failures. The experimental procedures and equipment described are grouped by type of reaction and are typical of the best results obtained in the attempted reductions.

Hydrogen and Carbon as Reducing Agents

Although reports of previous work, and calculations based on available thermodynamic data, indicated that neither hydrogen nor carbon would be satisfactory reducing agents, both were tried because they were two of the most common elements used in metallurgical reductions.

Attempts to reduce TiO_2 with hydrogen in a tube furnace at temperatures up to 1,250° C resulted in removal of only about 8 pct of the oxygen from the TiO_2 in the first hour or two. Thereafter, the rate of reaction dropped off rapidly. A marked change was noted in the appearance of the oxide treated. Before reduction, it was pure white, but at the end of the test, it was coal black. A rapid decrease in the rate of reduction after only a small portion of the oxygen had reacted indicated that the formation of metallic titanium by this method was not feasible.

When hydrogen was bubbled through $TiCl_4$ and the resulting gas and vapor passed through a silica tube heated to 875° C, a layer of lavender crystals, probably lower chlorides of titanium, formed in the cool end of the tube. There was no evidence of the formation of metallic titanium.

Although a number of earlier workers had reported that the metal produced by carbon reduction of TiO_2 was impure, the economy and simplicity of carbon reduction made this proposed process very attractive. In most carbon reduction tests, the reduction was made in two steps. First, TiC was made by reducing TiO_2 with carbon according to the reaction.

$$TiO_2 + 3C \rightarrow TiC + 2CO, \tag{14}$$

and then the metal was formed according to the second reaction

$$TiO_2 + 2TiC \rightarrow 3Ti + 2CO. \tag{15}$$

Initial attempts to produce TiC in a closed carbon crucible with no control of the furnace atmosphere yielded a brassy-colored sinter. The investigators assumed that the sinter was a nitride or cyanonitride. It was later found that homogeneous material having a composition corresponding approximately to TiO has a very similar color. It seems unlikely that the charges picked up enough nitrogen to form titanium nitrides in view of the large excess of carbon that was present. The product was probably a mixture of lower oxides and carbides. The formation of this sinter did, however, indicate the necessity for designing apparatus from which atmospheric contaminants could be excluded.

An induction-heated vacuum furnace was designed and additional tests to reduce TiO_2 with carbon were run, but the work was hampered by lack of a method for measuring high temperatures and by inadequate analytical methods. In some tests, MgO crucibles in the furnace almost disappeared, indicating that temperatures as high as 2,500° C were achieved. The analytical method used was ignition of the product to form TiO_2. From the increase in weight, an estimate was made of the titanium metal formed.

The production of relatively pure TiC was possible in the vacuum furnace. The sinter obtained was porous, crystalline, and steel gray in color. Although the first reaction, formation of TiC, was always conducted in a graphite crucible, techniques were developed for making MgO and ZrO_2 crucibles for use in the second reaction. Although the ZrO_2 crucibles were the best reaction containers available, they were not entirely satisfactory as cracks developed when they were heated through the transition temperature. The charge also attacked these crucibles. The best product contained about 70 pct Ti, 4 pct Zr, and a mixture of nitrides and lower oxides. Inability to prevent the formation of titanium compounds, then believed to be nitrogen, caused this method of reduction to be abandoned.

Metals as Reducing Agents

Calcium

The preparation of TiH_2 by reduction of the oxide with CaH_2 was a recognized step in the production of metallic titanium by the hydride process. This process was relatively expensive because of the cost of preparing CaH_2. A French patent *(57)* disclosed a method for preparing CaH_2 by reducing molten $CaCl_2$ with hydrogen. Such a process would be economically attractive and, accordingly, was investigated.

An experiment was conducted in which hydrogen was introduced below the surface of molten $CaCl_2$ held at 700° C in a nickel bomb. At the end of 96 h, no HCl was being evolved, and the reaction was assumed to be complete. The final product was a white crystalline material that was insoluble in water and dilute acid and contained 39.4 pct Ca. Digestion with hot concentrated HCl and HNO_3 resulted in 22.5 pct insoluble material. Hydrogen efficiency in the production of HCl was approximately 0.5 pct. This work was terminated because it appeared that the reaction did not proceed as claimed in the patent.

Aluminum

In a series of experiments in which aluminum was used as a reducing agent, both thermite-type and vacuum furnace reactions were attempted. Titanium dioxide, potassium fluotitanate (K_2TiF_6), and sodium fluotitanate (Na_2TiF_6) were used as sources of titanium. The temperatures produced by the reaction,

$$3TiO_2 + 4Al \rightarrow 3Ti + 2Al_2O_3, \qquad (16)$$

were not high enough to push the reaction to completion, and the slag formed was not fluid enough to allow the separation of any reduced metal that might have been produced. To overcome this difficulty, either barium peroxide (BaO_2) or potassium chlorate ($KClO_3$) was added to the charge as a booster, but a satisfactory separation was never made. In some of the experiments, a small button of fine-grained material separated out on the bottom of the crucible, but this material contained only up to 52 pct Ti.

In experiments conducted in the vacuum furnace, aluminum was added in excess of that required for reduction of TiO_2 in hope that the excess aluminum would distill away from the charge rather than alloy with the titanium. After reaction, no Al_2O_3 was found in the crucible. The sinter had the usual brassy color and contained 73 pct Ti.

When K_2TiF_6 was used a a source of titanium in vacuum-furnace aluminum reduction tests, the magnesium crucible was severely attacked. Material clinging to the sides of the crucible contained 77 pct Ti. Reduction of sodium titanate (Na_2TiO_3) with aluminum resulted in a final product similar to that obtained with the potassium compound.

Mixing the reactants in a crucible made it difficult to separate the reaction products, and a new series of tests was devised in which $TiCl_4$ was introduced as a gas over aluminum in a horizontal Pyrex glass tube. The tube temperature was held at 400° C for 14 days, then raised to 425° C for 6 additional days to volatilize the last of the $TiCl_4$. No evidence of metallic titanium was observed. It was probable that the reduction was only partially completed, resulting in a mixture of titanium lower chlorides, $AlCl_3$, and a titanium-aluminum alloy.

Magnesium

A similar attempt, substituting granular magnesium for the aluminum, was even less successful. At the temperature used, the magnesium grains became coated with a layer of solid reaction products, and the reaction stopped. The reaction temperatures were limited by the softening point of the Pyrex glass tube. Similar reductions at temperatures above the melting points of magnesium and MgCl and using other materials of construction would certainly have met with greater success had they been tried.

Sodium

A search of the available literature did not reveal any attempts to produce metal by reducing titanium sulfide with sodium. Sodium sulfide is easily fused and is water soluble. The method, therefore, appeared to offer a possibility for the production of titanium. A typical reduction was accomplished by reacting titanium sulfide with a 10-pct excess of metallic sodium in a nickel tray inside a small nickel reactor. The air in the reactor was replaced with hydrogen and the reactor was heated to approximately 600° C in an electric furnace.

At the start of the heating cycle, a rise in pressure occurred. This was followed by a period in which the pressure showed little variation. As the temperature continued to rise, there was a slow consumption of hydrogen. At the moment the reaction started, there was a sharp rise in pressure followed by a rapid drop that continued until the reaction was completed. The temperature at this point was usually about 525° C. No marked pressure change was then observed until a temperature of about 600° C was reached, the point at which TiH_2 started to decompose. This was indicated by a continuing pressure rise. The reactor was held at approximately 600° C for 15 to 20 min after the pressure showed no marked variation.

While cooling down, hydrogen was admitted to maintain a pressure of about 15 mm Hg. A rapid consumption of hydrogen always occurred when the temperature dropped to about 400° C, indicating the formation of NaH by the excess sodium in the charge and possibly also the absorption of hydrogen by the titanium. The resulting product was a porous, black sinter that ignited spontaneously on exposure to air. Therefore, it was necessary to flood the reactor with the leaching agent as soon as it was opened.

A number of variations in technique were tried. Increasing the quantity of sodium to 25 pct over stoichiometric did not affect the grade of the product. A test in which the reactants were placed in separate trays to introduce the reductant as a vapor was not successful. In tests in which hydrogen was replaced with helium as the reactor atmosphere, the titanium content of the leached product increased several percent.

Tests were made to determine the best procedure for leaching of the Na_2S or other soluble sodium compounds that might have formed. A vigorous effervescence accompanied by a strong odor of acetylene always occurred when the reduced charge was placed in water. The same effect, although not as violent, occurred when anhydrous alcohol was used as a solvent. When the leached and dried residue from a reduction made in a hydrogen atmosphere was heated in a tube with a small open end, a flammable gas was given off. Under the same conditions, material from a reduction made in helium exploded violently. In the first case, the product was probably a hydride, and in the second, finely divided metallic titanium.

In the four leach test runs shown in table 13, the reaction products were leached as described in the table and the solids separated by filtering or centrifuging. The residue was dried at 100° C for 1 h in a vacuum. In runs 1 and 3, where two leaching procedures are shown, the second treatment was made on a portion of the sample already leached by the first procedure. These tests demonstrated that acid leaching resulted in a higher titanium content in the residue. The best product contained 84.9 pct total Ti. The investigation was terminated because it appeared unlikely that a product of sufficient purity could be produced by this method. The probable high cost of preparing high-purity titanium sulfide also deterred further work on this type of reduction.

None of the Bureau's early work on displacement reductions, prior to investigation of the Kroll process, gave any evidence of production of a relatively pure metal. A summary of these tests, including the scale of the reactions, is shown in table 14.

Electric Discharge Decomposition

The fact that several stable gases are decomposed by the silent electric discharge suggested the possibility of decomposing titanium halides and, in particular, $TiCl_4$. It was realized that at best, only small amounts of titanium could be prepared at one time, but the desire for even a small amount of high-purity metal appeared to justify the investigation.

Experiments were conducted using a 7,500-V, 30-mA neon sign transformer and glass discharge tubes with cylindrical iron electrodes. A continuous discharge could only be produced in an atmosphere containing $TiCl_4$ when the distance between the electrodes was decreased to 4.5 in. The discharge was brilliant white fringed with red, but the brilliance of the light was soon obscured by deposition of a lavender coating on the walls of the tube. The heat of the arc caused the walls of the tube to soften and collapse.

Successively more sophisticated equipment was developed, finally resulting in the two decomposition apparatus designs shown in figure 27. A satisfactory discharge could be maintained in this apparatus at pressures up to 25 mm Hg. The water-cooled collector was

Table 13.—Composition of leached residues from sodium reduction of titanium sulfide, percent

Material leached and leaching procedure	Ti			S	Na
	Total	Soluble in HCl	Insoluble in HCl		
Typical residue from reduction in H_2 atmosphere:					
Water leach	71.3	70.7	ND	1.7	3.5
Anhydrous ethyl alcohol leach	76.1	73.8	ND	4.6	5.8
Typical residue from reduction in He atmosphere:					
Water leach	73.4	73.3	ND	ND	ND
Anhydrous ethyl alcohol leach	79.6	78.3	ND	ND	ND
Control run 1:					
Three 15-min leaches of anhydrous ethyl alcohol	75.9	73.1	3.4	3.1	3.2
Double treatment (as above) of anhydrous ethyl alcohol	75.8	73.9	3.2	2.5	2.8
Control run 2: Leached with 5-pct HCl until absence of H_2S odor	84.9	81.9	5.0	0	.27
Control run 3:					
1-pct HCl leach until absence of H_2S odor	78.2	68.1	6.8	5.1	.9
1-pct leach (as above) followed by 30-min leach in 5-pct HCl	72.6	66.8	8.1	4.5	.5
Control run 4: 5-pct HCl leach under vacuum	84.0	81.5	4.7	0	1.38

ND Not determined.

Table 14.—Displacement reduction methods tested in early titanium production attempts

Method	Procedure	Typical charge of raw material, g	Product
Hydrogen reduction of TiO_2	H_2 passed over TiO_2 in tube furnace at 1,250° C.	1.2 TiO_2	Black product; reduction equivalent to 8 pct of TiO_2 indicated.
Hydrogen reduction of $TiCl_4$	H_2 and $TiCl_4$ gases passed through tube furnace at 875° C.	Gases passed for 28 min	Practically no reaction.
Carbon reduction of TiO_2:			
Formation of TiC	TiO_2 and C reacted in covered crucible in induction furnace.	20-30 TiO_2	Brassy-colored sinter; no TiC formed.
	TiO_2 and C reacted in covered crucible in vacuum-induction furnace.	20-30 TiO_2	TiC sinter obtained.
Reduction of TiC	TiC and TiO_2 reacted in vacuum-induction furnace.	3-7 TiO_2 4-11 TiC	Brassy-colored sinter. Do.
Preparation of CaH_2 by action of H_2 on $CaCl_2$.	H_2 bubbled through $CaCl_2$ in Ni bomb at 700° C.	2.5 $CaCl_2$	Practically no reaction after 96 h.
Reduction of TiO_2 with Al	Thermite-type reaction in fireclay assay crucibles.	15-30 TiO_2	Brassy-colored sinter.
Do	TiO_2 and Al powder reacted in vacuum-induction furnace.	5 TiO_2	Do.
Reduction of K_2TiF_6 with Al	Fluorides and Al powder reacted in vacuum-induction furnace.	10 alkali titanium flouride	Do.
Reduction of $TiCl_4$ with Al and Mg.	$TiCl_4$ vapors passed over metal in Pyrex tube heated in tube furnace, 400° to 4,254° C.	8 $TiCl_4$	Unstable dark purple or gray residue, probably lower chlorides.
Reduction of Ti_2S_3 with Na:			
Preparation of Ti_2S_3	H_2S and CS_2 passed over TiO_2 in tube heated to 760° C	8-10 TiO_2	Ti_2S_3 product obtained.
Reduction with Na	Sulfide and Na reacted in Ni bomb.	1.5-3 Ti_2S_3	Leached residue contained up to 85 pct total Ti.

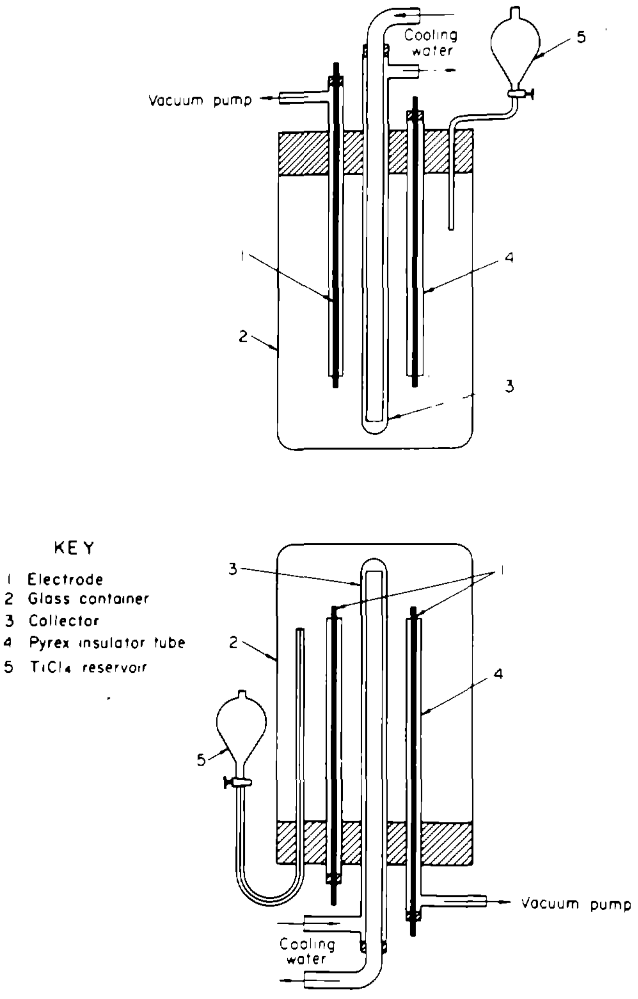

Figure 27.—Details of decomposition apparatus.

very effective. It gathered a deposit that was readily transferred to a weighing bottle. The apparatus did not become excessively hot, and it was possible to operate it continuously for several hours. Approximately 1 mL or 1.7 g of $TiCl_4$ was decomposed per hour. The final product of all electric discharge reductions was $TiCl_3$.

Titanium tetraiodide (TiI_4) was also tested in the discharge tube, and it reacted very similarly to $TiCl_4$. Only a small amount of work was done using the iodide because it was unstable and difficult to prepare.

Electrolysis in Aqueous Media

There were a few claims in the literature (*133*) that titanium had been produced by the electrolysis of aqueous solutions of its salts. A study was made of these claims and of similar ideas developed during the resulting investigations, although it seemed highly improbable that a metal as active as titanium could be deposited from an aqueous solution.

The aqueous electrolysis experiments were conducted in rectangular glass containers with a capacity of about 25 mL of solution. Electrodes were made of platinum and copper foil, depending on the corrosive character of the solution. Direct current power was supplied from a battery through a rheostat.

Attempts were made to electrolyze a number of solutions including the following:

Titanium hydroxide in saturated oxalic acid solutions.
Solutions containing titanium chlorides.
Titanium sulfate solutions saturated with boric acid.
Hydrochloric acid solutions of iron and titanium.
Concentrated titanium sulfate solutions.

No metallic deposits were obtained at the cathode in any of the experiments using a number of techniques.

Finally, the ammeter in the circuit was replaced with a galvanometer, and curves were plotted showing the relation between the voltage across the electrodes and the galvanometer readings. Curves representing the data derived by electrolysis of various aqueous solutions of titanium compounds compared with those derived from aqueous solutions of acids showed that the first break in every case was the decomposition potential for hydrogen. In view of this, production of titanium by electrolysis of aqueous solutions using insoluble solid electrodes seemed hopeless, and work in this direction was stopped.

The preparation of titanium amalgams had been reported in the literature (*73*). The suggested method appeared to be simple and, if successful, would offer a basis for preparing metallic titanium by decomposition of the amalgam. A special cell was constructed for these tests. The outer part of the cell was a 4-cm-ID glass tube drawn to a small opening at the bottom for introduction of the cathode lead. A small pool of mercury was placed at the bottom of the tube, and 35 mL of catholyte, consisting of a 7-pct solution of $TiCl_3$ in 2*N* HCl, was added. The anolyte, a 2*N* HCl solution, was contained in a 2-cm-ID porous Alundum cup. The platinum anode was immersed in the anolyte. After approximately 30 min of electrolysis, the mercury became so finely divided that it was no longer a conductor. The sludge proved to be finely flowered mercury that contained only a trace of titanium. When $TiCl_4$ was substituted for $TiCl_3$ in the cell, the solution became purple and then colorless. When HCl solutions without addition of titanium were electrolyzed, the same gray mercury sludge formed. The inability to separate titanium as an amalgam caused abandonment of investigations of aqueous electrolytes for production of titanium metal.

Electrolysis From Organic Solvents

In continued attempts to find a technique for producing titanium by electrolysis at ambient temperatures, the possibility of using nonaqueous solvents was investigated, and several such solvents were studied as possible ionizing agents for $TiCl_4$. Solutions of $TiCl_4$ in ethyl ether, benzene, pyridine, and acetic anhydride were either nonconducting or had very low conductivity. Ethylene diamine reacted with $TiCl_4$ to form dense brown fumes and a gummy brown solid. Glacial acetic acid formed an insoluble purple precipitate with $TiCl_4$.

A solution of $TiCl_4$ in ethyl acetate was a poor conductor when cold, but at about 100° C, 1 A at 12 V could be passed between 1-cm-square electrodes, 2 cm apart. A solution of 12.5 mL of $TiCl_4$ in 20 mL of ethyl acetate was electrolyzed in a U-tube between a carbon anode and a platinum cathode at a current density of 0.10 to 0.12 A/cm^2 and a temperature of 85° to 90° C for 140 h. No deposit was formed on the cathode, and analysis showed no concentration of titanium in the catholyte

Potassium titanium oxalate was found to be insoluble in the following organic liquids: Toluene, benzene, ethyl ether, ethyl acetate, pyridine, ethyl alcohol, acetone, amyl alcohol, and chloroform. Although the salt dissolved in glacial acetic acid and acetic anhydride, it did not ionize sufficiently to permit electrolysis.

Electrolysis From Molten-Salt Electrolytes

Electrolysis of TiO_2 in Molten Alkaline-Earth Halides

The electrolysis of molten alkaline-earth halogen salts containing TiO_2 to produce metallic titanium had been reported in the literature (*57, 99*). Such a method was economically attractive because it would permit the direct production of the metal from low-cost starting materials.

Calcium chloride ($CaCl_2$) was investigated as an electrolyte. Electrolysis of $CaCl_2$-TiO_2 mixtures in iron crucibles with an iron wire cathode for 15 min resulted in a sticky bath, and when the electrolyte was leached, no metal except iron from the crucible or cathode, or both, was found in the melt. Other tests using carbon anodes or introducing TiO_2 through a silica tube surrounding the cathode, or using porcelain crucibles in place of iron all resulted in failure.

Electrolysis tests in a carbon crucible heated by an induction furnace with the melt under a helium atmosphere gave a small formation on the cathode. This deposit did not appear to be metallic, but qualitative analysis showed that it contained a considerable amount of titanium. Work on this system was discontinued because no separation of titanium was accomplished in the electrolysis of $CaCl_2$ and TiO_2. Later work indicated that this may have been because no protection from atmospheric contamination was used in most of the experiments, and metal was reoxidized as fast as it was formed.

The system NaF-TiO_2 was briefly investigated. No metal was deposited, but leaching of the melt resulted in purple-colored solutions, indicating that there was some reduction to lower valency titanium. Potassium hydroxide (KOH)-TiO_2 melts, electrolyzed in a nickel crucible, did not give a deposit, nor did a solution of TiO_2 in potassium sulfide (K_2S). A mixture of sodium fluoride (NaF) and postassium fluoride (KF) was investigated as an electrolyte for TiO_2 decomposition in an attempt to use an electrolyte with a lower melting point. A charge of 204 g NaF and 92.5 g KF containing 4.82 pct TiO_2 was electrolyzed in a graphite crucible. The insoluble material that resulted from leaching the cathode deposit with cold water analyzed 48 pct Ti.

The final early attempts to produce titanium metal by electrolytic decomposition of TiO_2 were made using alkaline titanium fluorides as electrolytes. These tests were based on the idea that such systems might be analogous to those used for the electrolytic recovery of aluminum. Electrolyses were conducted in a carbon crucible that served as the anode, while a 0.25-in carbon rod served as the cathode. Electrolysis of potassium titanium fluoride (K_2TiF_6) or sodium titanium fluoride (Na_2TiF_6) without addition of TiO_2 showed that they were good conductors, but no titanium was produced in such an electrolysis. A mixture containing 75 pct K_2TiF_6 and 25 pct Na_2TiF_6 gave the lowest melting point and was used in the majority of the subsequent tests. TiO_2 content was varied from 10 to 20 g when 48 g of electrolyte was used. Current densities varied from 1 to 7 A/cm^2. In one electrolysis containing 10 pct TiO_2 in K_2TiF_6, black prismatic crystals, which contained 60.3 pct Ti and were probably TiO_2, formed on the underside of the crucible cover and were scattered throughout the melt. Microscopic examination of the globule of solid melt that hung to the cathode showed it to consist of alternate layers of gray melt and black crystals. A number of tests were run under varying conditions and although cathode accretions were obtained, the best deposits contained less than 50 pct Ti after leaching and no metallic deposits were obtained in any of the tests. Later work showed that many of the requirements for electrolytic production of titanium metal were not met. The raw materials used were not entirely free of moisture, and the cell was in contact with the atmosphere in most of the tests.

Electrolysis in Borax

Fused borax was tested as a possible elecrolyte. Potassium borate (KBO_2) was heated to 850° C but was too viscous to pour. The addition of K_2TiF_6 did not increase the fluidity, and a small addition of TiO_2 increased the viscosity. The lack of equipment to produce higher temperatures prevented any additional study of this system.

Electrolysis of Molten K_2S Containing Dissolved Titanium Sulfide

Preliminary investigation revealed that molten K_2S was a conductor and would dissolve as much as 10 pct titanium sulfide at 650° C without becoming viscous. The dissolved titanium sulfide distributed uniformly throughout the melt, and no undecomposed sulfide was observed when the melt was dissolved in water.

All electrolyses were made in porcelain crucibles heated in a resistance furnace. Melts were protected from oxidation by a flow of helium over the surface of the melt. A mixture of K_2S and titanium sulfide, containing about 2.8 pct Ti, was electrolyzed for 3 h at 2.7 A and 5.9 V using a carbon anode and a water-cooled iron cathode. No concentration of titanium around the cathode was observed. Surrounding the cathode with an Alundum tube to prevent mixing of the electrolysis products did not improve results.

Electrolysis of Alkali Titanium Fluorides in Fused Alkali Halides

The most successful of the early experiments on the production of titanium metal at the Bureau's station at Tucson, AZ, was the electrolysis of molten salt baths in which the source of titanium was either sodium or potassium titanium fluoride. Over 120 runs were made using this technique.

Apparatus

A cross-section diagram of the cell used in this work is shown in figure 28. The mixture of fused salts that formed the electrolyte (A) was contained in the turned graphite crucible (B), which in most of the experiments also served as the anode. The crucible and electrolyte were protected from atmospheric contamination by the mild steel chamber (C), which rested on the mild steel plate (D). An inlet pipe (F) was welded to the chamber (C) and was

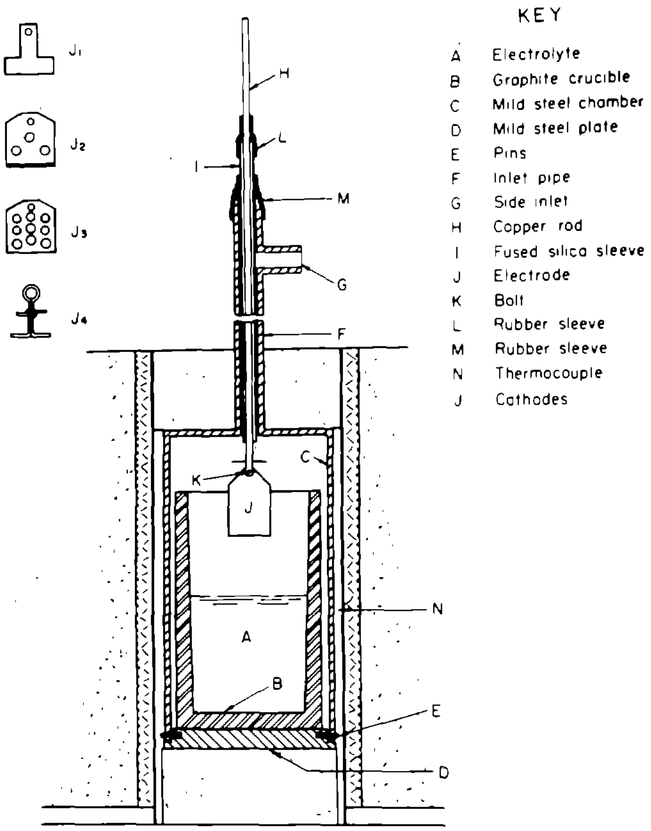

Figure 28.—Electrolytic cell.

provided with a side inlet (G) through which an inert or reducing gas was admitted during electrolysis. This gas passed down the inlet pipe, around the crucible, and out through the joint between the chamber (C) and plate (D). Electrical connection to the crucible was made to the inlet pipe (F). A ⅛-in copper rod (H) passed down through the inlet pipe (F) and was insulated from it by a fused silica sleeve (L). The lower end ot the copper rod was flattened and drilled so that the electrode (J) could be fastened to it.

Electrical connection to the electrode was made at the upper end of the copper rod (H). The electrode lead rod could be moved up and down in the sleeve so that the electrode could be immersed in the electrolyte or raised into the space above the bath at will. The cell assembly was heated in an electric furnace during electrolysis and could be lifted out for rapid cooling after the electrolysis was completed. Measurement of temperature was made by a thermocouple (N) in the space between the chamber (C) and the wall of the electric furnace.

Cell Operation

The cell was operated on a batch basis, as no means were provided for replenishing the electrolyte or changing the electrode while the cell was hot. In setting up for an experiment, the cell was cleaned and assembled outside of the furnace with the electrolyte in place; then connection was made with the source of gas to be used and the flow established at about 150 mL/min. As soon as sufficient time had elapsed for complete purging, the cell was placed in the furnace, which had previously been brought to operating temperature. After the electrolyte was melted, the movable electrode was lowered into the electrolyte and the power for electrolysis was turned on. The depth of the electrolyte was about 2 in, and the immersion depth of the electrode was about 0.75 in.

The period of electrolysis was based on the ampere-hours passed through the cell. By experience, it was found that about twice the theoretical ampere-hours gave the best results. When the period of electrolysis was too short, the melt had a lavender color, and when the period was too long, alkali metal was deposited at the cathode. As soon as the electrolysis had been completed, the flow of protective gas was increased, and the cell was removed from the furnace to cool. When the movable electrode was used as the cathode, it, and any adhering mass, were raised from the melt before the cell was removed from the furnace.

Both hydrogen and helium were tried as protective atmospheres. When helium was used, cell parts were severely corroded by the chlorine evolved in the electrolysis. Corrosion was negligible when hydrogen was used, probably because it reacted with the chlorine to form HCl, which was not as corrosive. Hydrogen was used in most experiments because funds were not available to construct a cell that would resist chlorine attack at the operating temperature. Although it was not recognized at the time, the use of hydrogen had the disadvantage that it must have introduced a considerable amount of hydrogen into the metal on the cathode, thus embrittling the deposited crystals and making them finer.

Relatively pure titanium deposits were obtained only when the crucible was used as the anode and molybdenum foil or wire as the cathode. Cathodes were designed, as shown in the upper left of figure 28, to give a high current density and, at the same time, furnish a large framework to support the mass of deposited crystals. Current densities of 1,000 to 3,000 A/ft^2 were obtained and the effect of variations of current density within this range was too small to detect. Total current ranged from 6 to 24 A, and the potential difference during operation varied from 3 to 4.5 V. Decomposition potential of the usual electrolyte was approximately 2.3 V at the beginning of electrolysis. Duration of electrolysis ranged from 12 min to 6 h.

A number of variations in operating technique were tried. In several tests, the molybdenum cathode was shielded by an Alundum cup. The shield filled with dark-colored crystalline material. The highest concentration of titanium was in some black material deposited on the outside of the shield, but no metallic particles were isolated. Other unsuccessful tests used carbon or titanium rods as cathodes and a carbon rod as an anode. No titanium was produced when the cell polarity was reversed, using the graphite crucible as the cathode. Molten metals were also tested as titanium collectors, using the reversed polarity setup. Zinc, aluminum, and magnesium were tested. Small amounts of titanium were found in the cathode material when using zinc, but the amount was too small to make practical the recovery of titanium by evaporation of the zinc.

Electrolyte Materials

In most of the experiments, the electrolyte was composed of equal parts by weight of sodium and potassium chlorides to which either sodium or potassium titanium fluoride was added. The average weight of the electrolyte was 330 g to which 15 to 20 g of fluotitanate was added. The only purification used in preparation of the salts was recrystallization and drying. No attempt was made to deoxidize or "condition" the bath except that in a few experiments, a small amount of titanium was placed at the bottom of the charge as a getter.

Changes in the composition of the electrolyte usually did not have any effect on the product. Variations in the relative amounts of KCl and NaCl controlled operating temperatures because of the changes in the melting point of the mixtures. Increasing the proportion of fluorine in the melt by addition of sodium or potassium fluorides did not improve operation. Potassium titanium fluoride was used in most of the tests because it was easier to prepare and purify. There seemed to be no difference in the results obtained from the sodium or potassium salts.

Most of the electrolyses were made at a temperature just above 660° C, which was the melting point of the electrolyte. A few were made at 720° C, and the higher temperature appeared to produce larger crystals. However, the protective chamber oxidized so rapidly at the higher temperatures that it was not feasible to use them. The titanium content of the bath was varied from 1 to 3 pct. Within these limits, no effect was noted on the product.

Cathode Deposits

In the successful experiments, the titanium was obtained as a mass of fine crystals that adhered to the cathode strongly enough that the whole mass could be lifted out of the electrolyte for partial draining and cooling. Figure 29 shows a deposit on the earliest type of cathode used, an inverted T cut from molybdenum foil. Below it is the broken face of the melt from which it was taken.

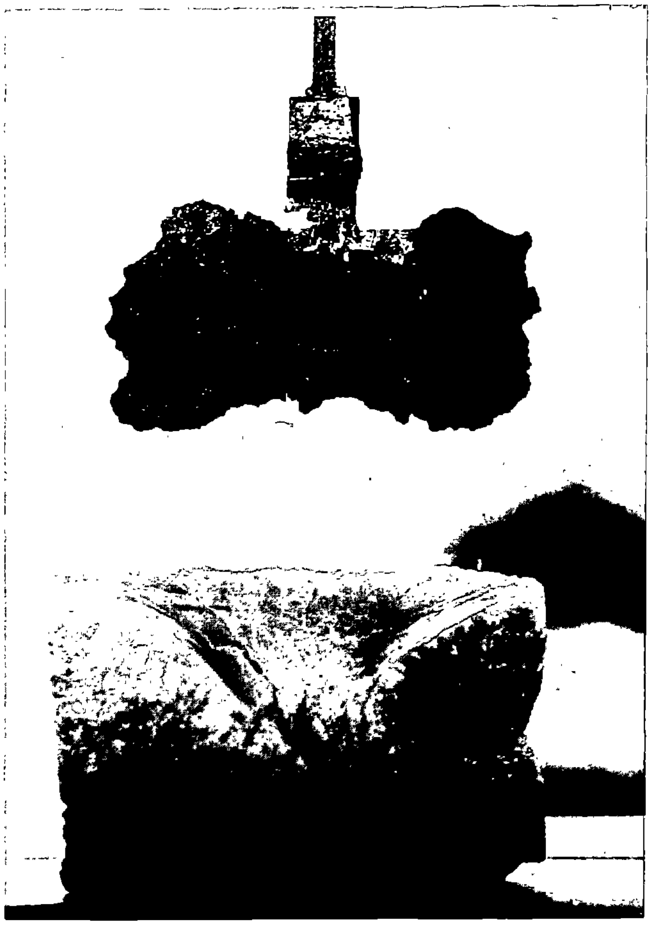

Figure 29.—Deposit on J1-type cathode with solidified electrolyte beneath.

Because of the finely interfaced nature of the deposited crystals, drainage of the electrolyte was poor, and much of it remained with the deposit. The weight of the mass adhering to the cathode was from 6 to 10 times the weight of the metallic crystals it contained. The entrapped electrolyte was dissolved from the cathode deposit by suspending it just under the surface of water in a beaker and letting it stand over night. The titanium crystals were separated from the leach solution, broken apart, and washed with distilled water. The washed crystals were air-dried, and physically admixed impurities, such as carbon, were removed by float-sink separation with acetylene tetrabromide ($CHBr_2CHBr_2$). After the heavy fraction had been washed free of the heavy liquid with benzene, it was dried and separated into three fractions: Plus 200 mesh, minus 200 plus 325 mesh, and minus 325 mesh. Figure 30 shows some of the finished leached product and a small compact pressed from it.

Quality of Metal

The test methods available at the time were not such as to permit a precise evaluation of the quality of the metal produced. No equipment was available for sintering or melting the crystals obtained, therefore, the hardness testing technique, which was later proven to be the simplest control method, could not be used. The product was evaluated by chemical analysis using a technique in which a sample was treated with strong HCl, the insoluble matter filtered off, and the titanium and iron precipitated as hydroxides. The content of titanium plus iron in the electrolytic product was estimated by weighing the ignited precipitate. Table 15 shows the analysis of some typical runs using this method of evaluation. In successful tests, almost all of the titanium added as the complex fluoride was recovered as metal.

When suitable equipment became available, some of the plus 200-mesh fractions of the crystals produced at Tucson were composited and tested using the button melting and analytical testing procedures in use in 1954. Brinell hardness of the melted button was 247, and the metal contained 0.70 pct Fe, 0.007 pct N, 0.30 pct O, and 1.27 pct H.

Work on the electrolytic production of titanium metal was terminated in favor of development of the Kroll manganese reduction process. From 1941 until electrolytic work was resumed in 1952, all of the Bureau's research on the extractive metallurgy of titanium was concentrated on chemical reduction methods.

DEVELOPMENT OF MAGNESIUM REDUCTION OF TITANIUM TETRACHLORIDE

After consideration of virtually every process proposed for the production of metallic titanium, and evaluation of the research previously described, it was concluded that the magnesium reduction of $TiCl_4$ as described by Kroll (*113*) was the most practical for

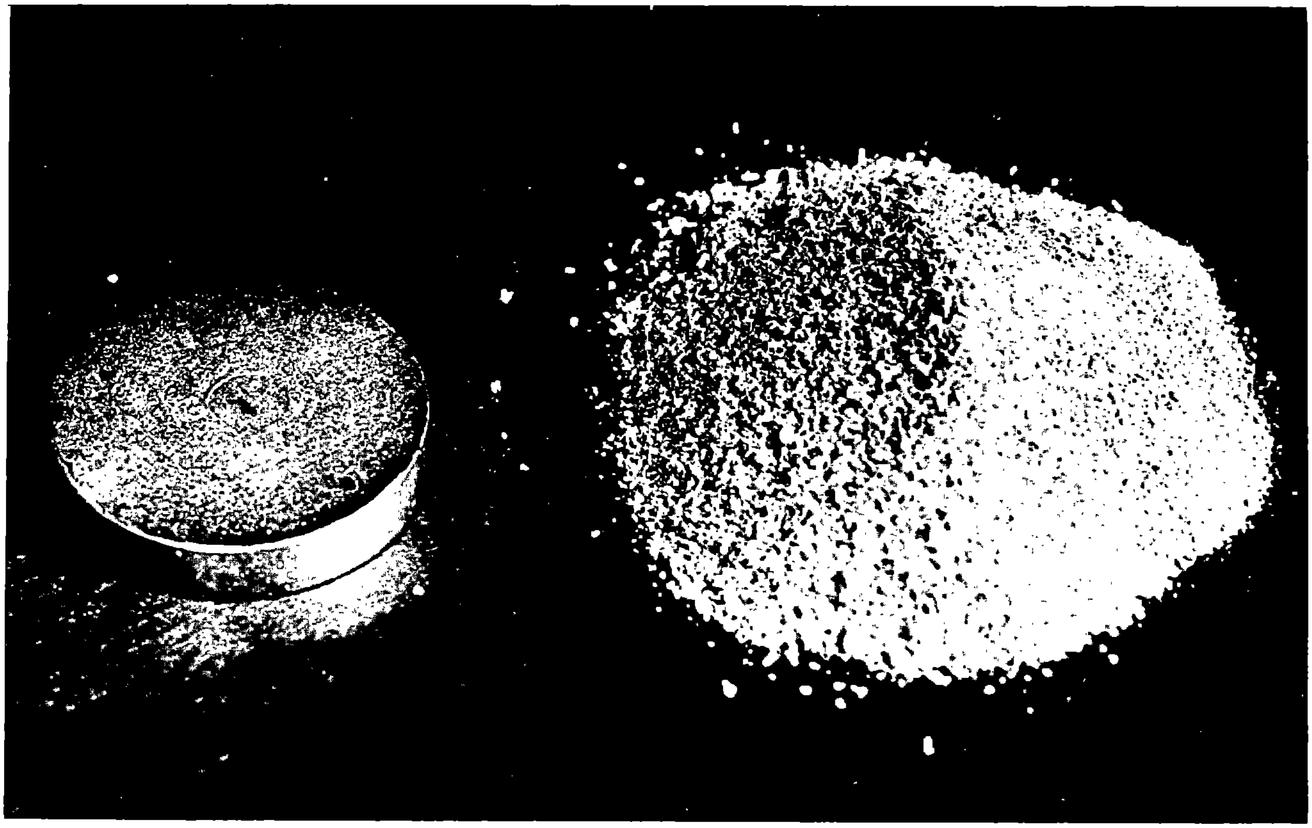

Figure 30.—Pressed compact (left) and titanium powder (right) of type from which it was pressed.

Table 15.—Recovery, size distribution, and analysis of titanium powder from molten-salt electrolysis of alkali titanium fluorides

	Run			
	28	30	32	33
Ti in charge . . . . .g. .	8.76	10.95	7.93	8.90
Ti in deposit . . . . .g.	8.4	9.7	8.1	8.8
Recovery . . . . .pct. .	95.9	88.65	102.0	98.9
Plus 200 mesh:				
Metal . . . . .g. .	1.9	1.6	3.5	3.4
Ti and Fe . . . . .pct. .	100.6	99.8	99.9	99.4
Minus 200 plus 325 mesh:				
Metal . . . . .g. .	4.0	4.2	2.8	3.4
Ti and Fe . . . . .pct. .	98.6	96.5	96.6	97.6
Minus 325 mesh:				
Metal . . . . .g. .	2.5	3.9	1.8	2.0
Ti and Fe . . . . .pct. .	95.2	74.1	93.4	95.2

expansion to commercial production. Briefly, the process consists of the reduction of $TiCl_4$ with molten magnesium at a temperature of about 800° C. At the conclusion of the reduction, the reaction mass consists of titanium, magnesium chloride ($MgCl_2$), and unreacted magnesium. Separation of the reaction products may be accomplished either by leaching or distilling the $MgCl_2$ and magnesium from the titanium. In all of the early Bureau research, separation was by the leaching procedure.

The main reaction forming titanium metal may be written

$$2Mg + TiCl_4 \rightarrow 2MgCl_2 + Ti. \qquad (17)$$

When all of the readily accessible magnesium has been reacted, the possibility of other reactions increases considerably. Among these might be

$$Mg + 2TiCl_4 \rightarrow MgCl_2 + 2TiCl_3 \qquad (18)$$

$$Mg + TiCl_4 \rightarrow MgCl_2 + TiCl_2, \qquad (19)$$

$$Ti + 3TiCl_4 \rightarrow 4TiCl_3, \qquad (20)$$

$$Ti + TiCl_4 \rightarrow 2TiCl_2. \qquad (21)$$

Any trichloride formed may also dissociate to form a mixture of dichloride and tetrachloride under favorable temperature conditions:

$$2TiCl_3 \rightarrow TiCl_2 + TiCl_4. \qquad (22)$$

Formation of lower chlorides is undesirable, not only because they represent a loss of titanium, but also because after the reaction vessel is opened, they react with the atmosphere, often igniting spontaneously and contaminating any titanium metal in the immediate vicinity. In the Bureau's research, formation of lower chlorides was minimized, mainly by having enough magnesium present to react with the $TiCl_4$ as it was added.

The reaction of $TiCl_4$ with magnesium is exothermic, and the heat released is about 2,786 Btu/lb of titanium produced if the tetrachloride is added as a liquid and the magnesium is molten. This heat of reaction must be dissipated to avoid overheating of the reduction equipment.

Preliminary Reduction Tests (*40*)

A schematic diagram of the apparatus used in the preliminary studies is shown in figure 31. Parts of the apparatus and their functions are shown in the sketch.

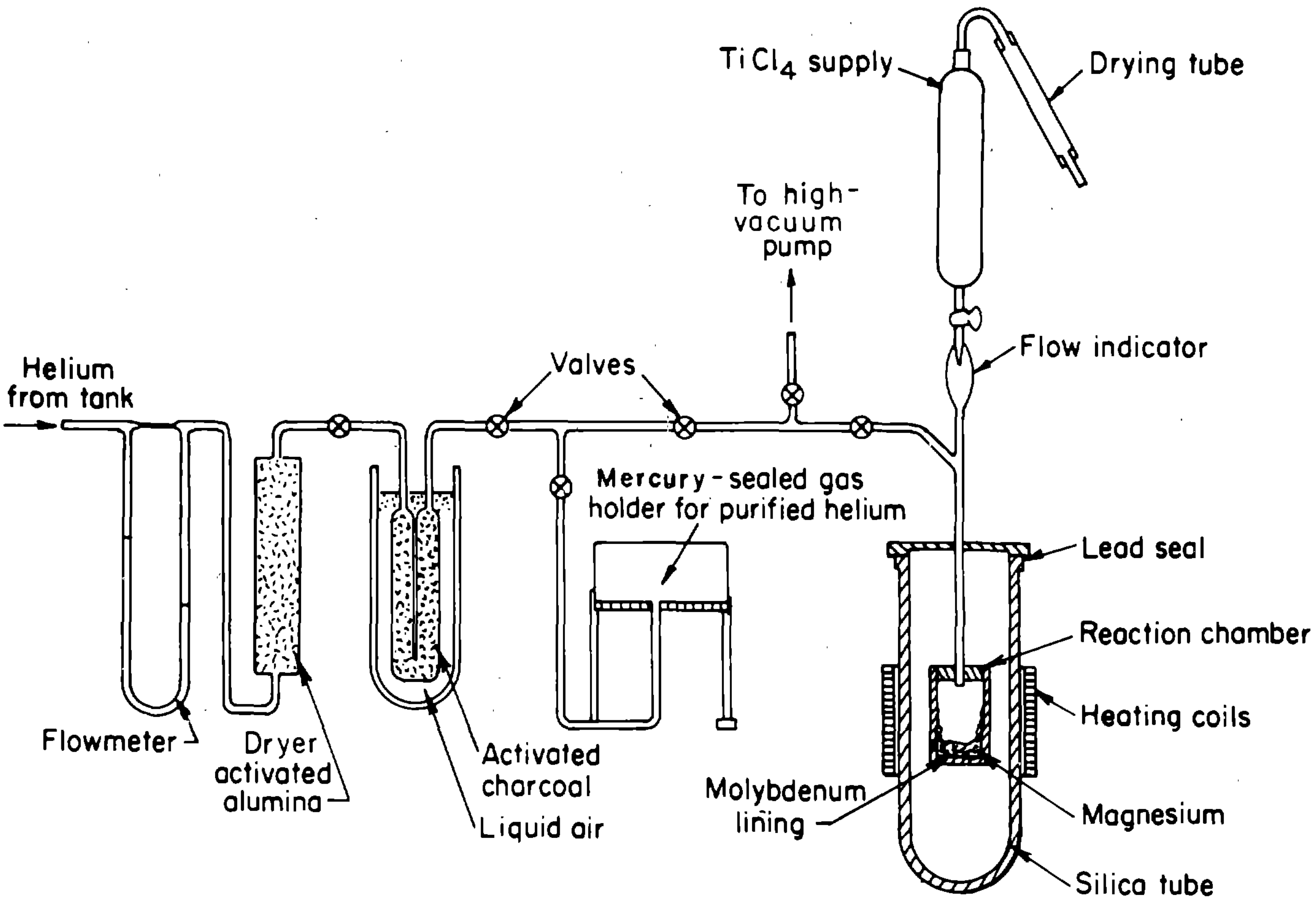

Figure 31.—Apparatus for small reductions.

The weight of titanium produced per batch was determined by the size of the reduction crucible, which at first was about 1.25 in. in diam and 2 in high. Although small, this was sufficient for the initial purpose. The Kroll technique was followed, except for the method of cleaning and preparing the reduction chamber for each run. This procedure consisted of heating the reduction chamber to a temperature of about 500° C in an atmosphere of hydrogen, completely reducing any iron oxide present, and then replacing the hydrogen with purified helium.

The chamber was then loaded with carefully cleaned pieces of magnesium, evacuated, filled with purified helium, and heated to about 750° C by induction. Titanium tetrachloride was then allowed to drip onto the molten magnesium in the reduction chamber. The temperature was allowed to rise gradually to about 1,000° C, usually reaching this point at the time that all of the tetrachloride has been added. The crucible was then allowed to cool with its contents protected from oxidation by the helium atmosphere. The reaction mass was then dug out of the crucible, mixed with cold dilute HCl, ground, and releached to obtain a minimum of residual magnesium. With this first apparatus, titanium yield was about 70 pct and magnesium efficiency about 60 pct.

Expansion to 15-lb Reduction Batches (*40-41*)

The preliminary tests were sufficiently encouraging to justify considerable expansion in the scale of the work, and the size of the reduction apparatus was increased stepwise to a capacity of 15 lb of titanium per batch.

In the course of this expansion, various changes in apparatus and technique were found desirable. It was found that an unlined iron crucible could be used instead of the molybdenum-lined crucible initially used, as long as the temperature was not allowed to rise much above 900° C in the course of the run. Higher reaction temperatures resulted in a decided increase in the iron content of the product. Tank helium, containing about 1.5 pct Ni, was used directly because purification was impractical for the large apparatus. However, the limited quantities of nitrogen introduced from the static helium atmosphere in the reduction chamber were not sufficient to cause appreciable harm to the titanium.

The apparatus finally adopted for the 15-lb runs is shown in figure 32. The inside surfaces of the reaction chamber, which was 12 in. in diam by 14 in high, were carefully cleaned by pickling in dilute HCl, scraping, and polishing with emery cloth. The cover was then welded on, and the assembly was filled with hydrogen and heated to 500° C to reduce the oxide formed on the interior surfaces by the welding.

After cooling, 20 lb of carefully cleaned magnesium ingots were introduced through the inlet tube, and the assembly was heated to 150° C and evacuated to remove adsorbed gas from the chamber walls and the magnesium. Helium was introduced, the pressure was allowed to build up to slightly above atmospheric, and the temperature

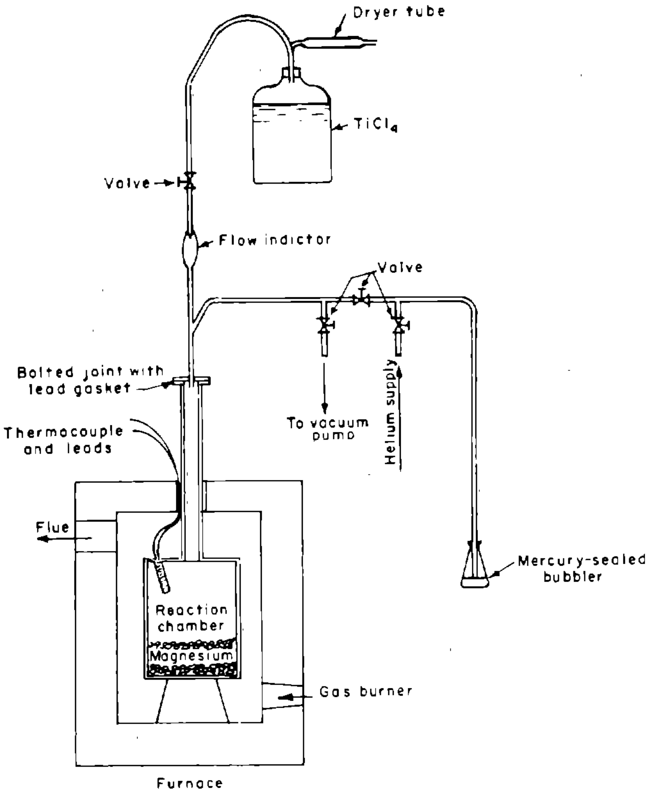

Figure 32.—Reduction unit for 15-lb runs.

was raised to about 750° C. Liquid $TiCl_4$ was run into the reaction chamber, slowly at first, and then as rapidly as the reaction would permit. The heat evolved was sufficient, after the reaction got under way, to maintain the temperature at the desired point without external heating for about two-thirds of the run.

In the latter portion of the run, no doubt because of the lack of magnesium available at the reaction surface, the rate of reaction decreased. This reduced the rate at which $TiCl_4$ could be added, and external heating then became necessary. The normal practice was to allow the temperature to rise gradually from the initial 750° C to 900° C, and to maintain this temperature for about 0.5 h after all of the $TiCl_4$ had been added. A slight positive pressure of helium was maintained in the reaction chamber during the entire run.

The steps through which the size of the equipment was increased to produce 15 lb of finished powder per run are indicated in table 16. In general, very little difficulty was encountered in increasing the size of the equipment, and in fact, a number of advantages were observed. It was more convenient to handle and measure larger amounts of $TiCl_4$, the larger inlet tubes permitted the use of larger pieces of magnesium, which were easier to clean, and there was less spattering of the reaction mixture on the lids of the larger reaction chambers, thus decreasing the danger of stoppage of the $TiCl_4$ inlet.

Table 16.—Data on reduction process

	Bureau of Mines				Kroll
Reduction pot size .... in	1.5	3.5	6	12	NA
Temperature range .... °C	750-1,000	760-850	740-820	800-870	740-1,068
Mg used .... g	21	200	1,500	[1]21.5	360
$TiCl_4$ added .... g	63.8	638	4,730	[1]62.5	1,138
Time of $TiCl_4$ addition .. min	66	145	140	205	110
Ti powder produced .... g	11.8	144	1,067	[1]14.5	284
Ti-TiCl ratio	0.19	0.22	0.22	0.23	0.25
Theoretical yield .... pct	73	89	89	92	98
Ti-Mg ratio	0.56	0.72	0.71	0.68	0.79
Mg reduction efficiency .pct	57	73	72	69	80

NA Not available.
[1] Pounds.

The reduction efficiency increased with increased scale. As shown in table 16, the efficiencies, particularly those of magnesium utilization, were lower than those reported by Kroll. Investigation showed that some of the magnesium was held between the crystals of deposited titanium. Although no alloying appeared to be involved, the adhesive forces apparently were strong enough to prevent the magnesium from rising to the surface of the reaction mass where it could come into contact with $TiCl_4$. It was possible to force the magnesium out by raising the temperature, but in an unlined reduction pot, this increased the iron content of the product. The lower magnesium efficiencies obtained in this work, when compared with those reported by Kroll, were doubtless because of lower reaction temperature.

The purity of the product was chiefly controlled by the purity of the raw materials; purified $TiCl_4$ was used. The magnesium used in the early work was redistilled, but later, high-grade commercial ingot metal was found to be quite satisfactory.

Precise analytical methods for determining small amounts of all of the impurities were not yet available, so it was not possible to determine accurately the purity of the material produced. However, qualitative spectrographic examination permitted estimation of the metallic impurities present. In general, the same impurities found in the magnesium were also present in the titanium. The chief impurities were iron, silicon, magnesium, oxygen, nitrogen, and hydrogen. The presence of the magnesium, as previously noted, was due to entrapment in the reaction mixture. Iron contamination was caused by reaction with the chamber walls, the boring of the mix from the chamber, and grinding of the product. The free iron could be removed by magnetic separation, as could the major portion of the titanium-iron alloy formed on the walls of the reaction crucible. However, complete removal was not achieved, and some iron was found in all of the powder produced.

Pilot-Plant Reduction (*61, 214*)

Following the successful reduction to produce 15-lb batches, development work on the production of titanium was transferred in 1944 from Salt Lake City, UT, to Boulder City, NV, and a pilot plant was constructed at that location in which batch size was expanded to 150 lb and later to 225 lb. Major emphasis in the pilot-plant operation was on the development of procedures that would permit regular production of ductile metal. A standardized technique was developed, and changes were adopted only after the effect on the product had been determined and found to be desirable. The procedures and equipment were basically scaled up versions of those developed for the small batches. Principal improvements were the development of a method for removing most of the molten $MgCl_2$ formed during the reduction by tapping it off, use of a "dry room" for removal of the reaction mass, and use of vacuum distillation, rather than leaching, for separating reaction products.

The tapping operation resulted in large savings in labor, materials, and equipment in handling and purification of the reaction mass. A controlled atmosphere room with low humidity was constructed in which the reaction vessel was opened and the reaction mass removed. This minimized absorption of moisture by the magnesium chloride and thus permitted development of a vacuum distillation method for separation of reaction mass constituents. During operation of the plant, both leaching and distillation techniques, as will be described later, were employed for separating the reduction products.

Preparation of Raw Materials

Ingots of standard magnesium, which met the requirements of ASTM designation B92-45, were used. The ingots were prepared by boring holes in the top surface as needed to open up covered shrinkage cavities. Then the ingots were pickled for a few minutes in dilute HCl, washed in cold running water, and then dried.

Purified $TiCl_4$, prepared in the pilot plant previously described, was used. Hydrogen sulfide was used in the chemical reaction step of the tetrachloride purification.

Reduction Equipment

The principal items of equipment used in the pilot plant reduction of $TiCl_4$ were

1. A reduction chamber.
2. A furnace to heat the chamber.
3. Welding and grinding equipment and a rolling machine positioner used in sealing and opening pots.
4. A lathe to remove the reaction mass.
5. A controlled atmosphere dry room in which to perform the lathing operation.
6. Vacuum pump for evacuating the reduction chamber.
7. Magnesium cleaning equipment.
8. Purified $TiCl_4$ feed tanks.
9. Vessels for storage of chips produced in lathe operation.

Figure 33 *(61)* is a sectional drawing of the 225-lb per batch reduction chamber and furnace. A detailed description of the reduction apparatus follows.

The reduction chamber (0) was a 30-in-high, 30-in-OD vertical cylinder (1) with a welded-in bottom (2) and a flange (3) welded to the top of the cylindrical section. A tapping block (4) made from a piece of 2-in shafting was welded to the outside of the chamber, so that a 1-in taphole drilled through the block and chamber wall was flush with the chamber bottom. The taphole was closed with a water-cooled bar (5).

The lid (6), cut from 0.5-in plate, matched the diameter of the flange (3) on the chamber. Three columns were welded over appropriate holes on the lid. Two of the columns (7) were made from 2-in pipe 24 in long and were used essentially for poking. The center column (8) was a piece of 5-in pipe 38 in long, encircled near the upper end by a water jacket (9), and sealed with a lead gasket and bolt-on cover. Through the cover passed the supply lines for helium (10) and $TiCl_4$, as well as the line (15) for equalizing pressure between the chamber and the $TiCl_4$ supply drum. Liquid $TiCl_4$ was supplied to a revolving feeder (11) and stationary feed pipe (12). The rotary feeder arm (13) was revolved at 2.1 r/min by a suitable belt drive. Two packing glands (14) made a gastight seal around the rotating parts. The furnace used to heat the reaction chamber was a vertical, cylindrical structure having a heated chamber about 48 in. in diam and 4.5 ft in height. The furnace was fired by two oil burners.

Temperatures were measured by five Chromel-Alumel thermocouples, three (23-25) of which were placed against the outside surface of the reaction chamber at points 10 and 14 in from the bottom of the chamber and on the chamber lid. One thermocouple (26) was embedded in the disk (20) and another (27) passed through the lid of the 5-in column and extended to a point about 0.25 in below the chamber lid. One thermocouple (23) controlled one of the oil burners to maintain a substantially even temperature at that level of the chamber. Because none of these thermocouples were actually in the reaction zone, they gave only an indication of the true temperatures inside the chamber. Nevertheless, the indicated temperatures were useful aids in maintaining a definite schedule for conducting the reduction operation.

Other features of the reduction apparatus included firebrick furnace walls (16) and bottom (29), furnace baseplate (17) and reinforcing bands (18), reaction chamber support blocks (19), furnace lid (21), and slag launder pipe (22).

Standardized Operating Procedures

After appropriate cleaning, the reduction chamber or pot was loaded with cleaned magnesium ingots. Two methods of sealing the lids to the pots were employed. In the early work, flanges of the pot and lid were bolted together by 42 0.75-in-diam bolts. One copper and one iron gasket, which were formed by bending wire into appropriate size circles and welding the ends, were used. The iron gasket, made of slightly smaller diameter wire, was placed inside the copper gasket and served as a vapor barrier for the copper. The seal was provided by the compression and flattening of the copper wire. The second method of attaching the lid was by a light surface weld around the entire perimeter of the flanges. Practice proved the welded joint most satisfactory. With new pots, neither method showed much advantage; but as the pots were used, warpage and distortion took place, and this made it necessary to level the flange faces before gasket sealing was possible. Weld seals were satisfactory for the life of the equipment.

The sealed assembly was placed in the furnace, the insulated furnace lids were closed, and the helium and water lines were connected. The reduction chamber was evacuated and filled with helium twice. After the second evacuation, a helium pressure of 0.5 lbf/in^2 above atmospheric was maintained in the chamber by using a pressure regulator on the helium supply line.

The burners were lighted, and heat was supplied until roughly 20 to 30 pct of the magnesium had been melted. Then, tetrachloride feed was started at a rate of about 3 gal/h. Frequently, a period of inactivity occurred, and the tetrachloride added to the chamber vaporized but did not react. The resulting pressure increase was relieved by opening the vent line and allowing gas to escape through the equalizer line (15). When pressure stability was attained, the feed rate was increased to approximately 15 gal/h. Some of the heat developed in the early part of the reduction by the exothermic reaction was used in melting the magnesium. After that, temperature was controlled by a combination of oil burner control, furnace draft, rate of feed, and area of feed distribution.

Some control of temperature was essential. The temperature had to be maintained between the melting point of $MgCl_2$ (712° C) and the iron-titanium eutectic temperature of 1,085° C. If the temperature of the reaction

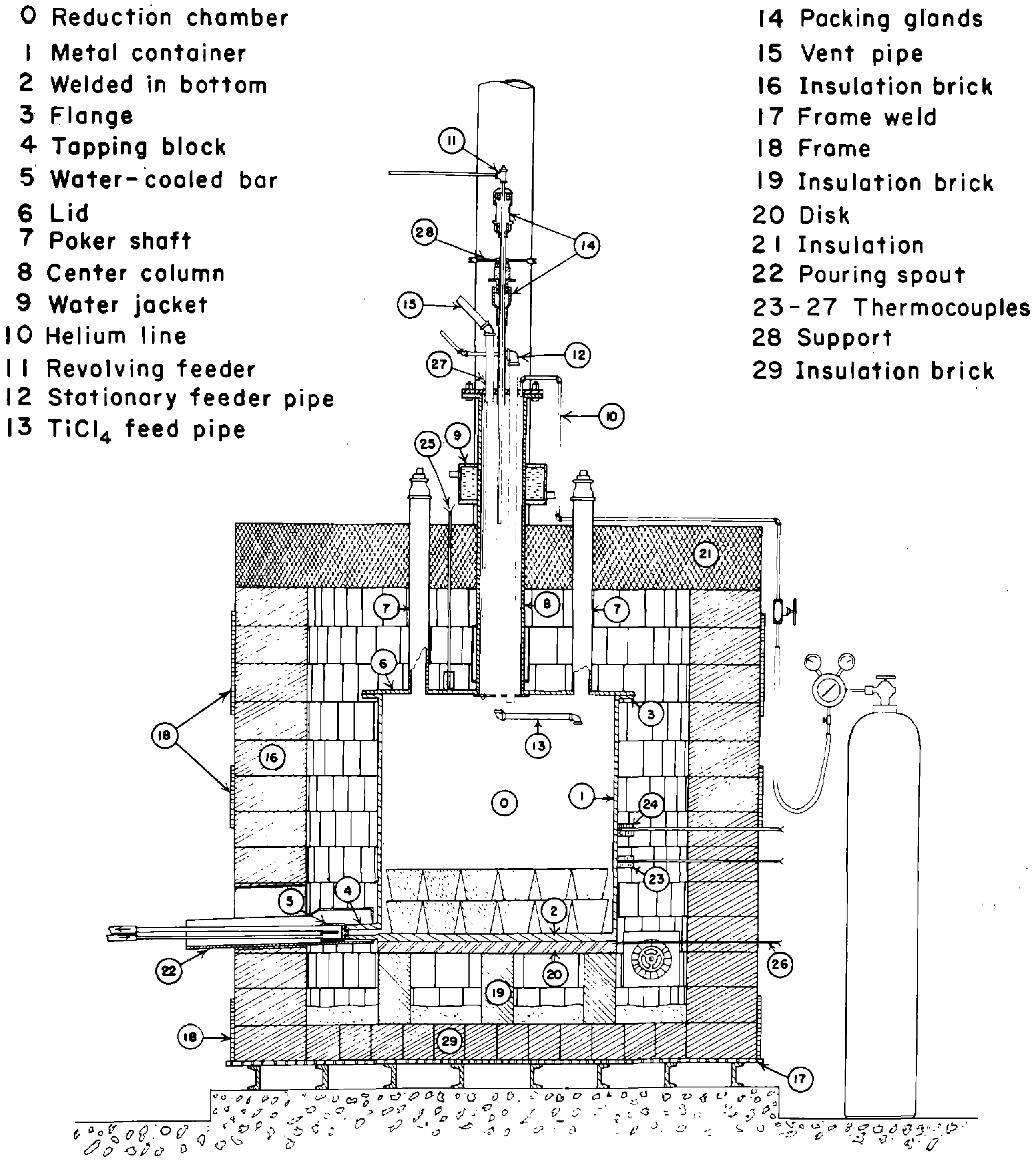

Figure 33.—Sectional drawing of titanium reduction chamber and furnace.

mass dropped below the melting point of $MgCl_2$, there was a drastic drop in the reaction rate. High temperatures produced several undesirable results: The iron-titanium eutectic alloy would start to form, resulting in a high iron content in the product and accelerated corrosion of the reduction equipment; vapor pressure of the magnesium increased with consequent reaction and deposition of titanium in the upper part of the pot and on the lid; $TiCl_4$ was reduced by the iron of the equipment causing the formation of lower chlorides of titanium and iron chlorides, which contaminated the product.

As the reaction proceeded, the reaction rate decreased at abrupt intervals, undoubtedly because of the decreased availability of magnesium, thus necessitating a reduction in the rate of feeding tetrachloride. The first reduction came when approximately 40 pct of the feed had been added, the second at 60 pct, and a third when 75 pct of the predetermined amount had been added. Molten $MgCl_2$

was tapped from the pot when 60 pct of the $TiCl_4$ had been added. Removal of the $MgCl_2$ maintained contact area for the remaining magnesium and permitted acceptable tetrachloride feed rates.

As available magnesium was used up, less of the added tetrachloride reacted according to reaction 17, and more reacted according to reaction 20. By experiment, it was found that, with care, tetrachloride equivalent to 85 pct of the stoichiometric quantity required to react with the magnesium usually could be added without appreciable loss of titanium as lower chlorides, although there was some condensation of lower chlorides on the upper walls of the reaction chamber. Addition of $TiCl_4$ equivalent to 90 pct of the original charge of magnesium usually resulted in appreciable amounts of titanium in the $MgCl_2$. Use of tetrachloride equivalent to 93 to 95 pct of the magnesium resulted in still greater losses of titanium as lower chlorides. Apparently, it was not possible to utilize the last 10 pct of the magnesium, although, as will be described later, many attempts were made to do so.

As previously mentioned, the presence of lower chlorides of titanium was undesirable for two reasons. First, they were partly soluble in molten $MgCl_2$ resulting in a loss of titanium. Second, they tended to condense in the column, on the underside of the lid, and on the upper side walls. These compounds, exposed to air when the reaction chamber was opened, oxidized with the evolution of considerable heat and sometimes ignited spontaneously, ruining any titanium in the near vicinity.

On completion of tetrachloride feeding, the $MgCl_2$ was again tapped. The reaction chamber was held at temperature for about 1 h to allow completion of the reaction, coarsening of the structure of the sponge, and to facilitate drainage of $MgCl_2$ into the bottom of the chamber. A final tap was then made. Approximately 90 pct of the $MgCl_2$ produced was removed in the tappings.

The color of a sample of the $MgCl_2$ slag was a good indication of its titanium content. Even a few tenths of a percent of trivalent titanium produced a characteristic lavender color. Samples of slag were taken for determination of titanium content only when the slag was colored.

After the run had been completed, the reaction chamber was allowed to cool in the furnace until the temperature had dropped below the freezing point of the $MgCl_2$. Then the pot was disconnected and lifted from the furnace to cool to room temperature. A helium atmosphere was maintained in the reactor until it was cold. After the pot had cooled to room temperature, the weld that closed the seam between the pot and the lid was ground away while the pot revolved slowly on rolls. The assembly was then taken to the dry room where the lid was removed, the pot was mounted in a large lathe, and the charge was bored out. The crude titanium was recovered in the form of chips that could be refined either by leaching or by vacuum distillation, as desired.

When the sponge was to be refined by vacuum distillation, precautions were required to minimize hydration of the $MgCl_2$ during the boring operation. Otherwise, when the hydrated material is heated, at least part of the absorbed water reacts with the titanium, increasing its oxygen content and hardness. To minimize moisture pickup, a stationary hood, resting on the ways of the lathe, was placed over the open end of the pot during turning. By use of the dry room and this added shielding of the boring operation, absorption of moisture was reduced so that the product did not harden appreciably, even when the pots were reused without cleaning and the chips of crude titanium were purified by vacuum distillation rather than by leaching.

Operating Data—Standard Procedure

The main objective of the pilot-plant operation was to supply titanium in a pure enough state to determine its physical properties, fabrication characteristics, and potential applications as a structural metal. Every effort was made to produce a product as pure as possible within limits of reasonable production costs. Table 17 is a summary of the operating data from 10 consecutive runs made in the smaller (150-lb batch) equipment. The operating procedures described in the preceding section were employed. Table 18 is the log of a typical reduction run in the larger (225-lb batch) equipment.

Experimental Modification of Operating Procedure

Experimental reductions were made in the 150-lb batch equipment in an attempt to make the process simpler and more efficient.

A number of experimental reductions were made in an attempt to utilize magnesium more efficiently. A relatively slow feed rate of 8 gal/h during the first part of the run was tried on the theory that a low feed rate would allow more time for separation of magnesium. It had the opposite effect, however, promoting the formation of hard horizontal layers in the reaction chamber, and thus completely preventing entrapped magnesium from rising to the surface. A relatively high feed rate of 20 gal/h showed less tendency to form impermeable crusts, but resulted in the evolution of so much heat that difficulty was experienced in holding the temperature within limits. The high feed rate also caused a larger amount of material to stick to the lid.

Use of very low temperatures (750° C) resulted in sponge more porous than usual, and utilization of magnesium tended to be lower. Maintenance of the temperature near 900° C, especially during the latter half of the run, made it much easier to attain 90-pct Mg utilization, but increased the iron content of the titanium several hundredths of a percent.

Feeding the tetrachloride in vaporized form, use of a stirrer, and vibration of the 5-in column were all tried, but

Table 17.—Summary data from 10 consecutive reductions in 150-lb batches

Item	Max	Min	Av
Charge:			
Mg ... lb	185	176	180.7
$TiCl_4$ ... lb	834	793	810.1
Ti content of added $TiCl_4$ ... lb	164	152	152.6
Calculated Mg utilization ... pct	92	88	89.4
Product:			
Slag ... lb	533	440	485.3
Reaction mass ... lb	359	256	312.1
$MgCl_2$ ... pct	55.1	42.9	49.1
Mg ... pct	7.5	4.8	5.9
Ti ... pct	39.8	51.2	44.9
Ti lost, lb:			
In slag	48	0	1.6
In fires	50	0	8.1
$TiCl_4$ addition rate, gal/h:			
First half	16	16	16
Last half	10	6.33	9.26
Reduction time, min:			
Preheat	105	70	85.5
$TiCl_4$ addition	285	225	239.9
Postheat	70	30	59.3
Temperature midpot, °C:			
First half	970	810	858
Last half	880	1,000	902
Helium used ... ft^3	292	53	110.4
Fuel oil used ... gal	22	17	19.5

Table 18.—Log of a typical 225-lb titanium reduction run

Operation	Time	$TiCl_4$ addition rate, gal/h		Total $TiCl_4$ added, lb	Temp at thermocouple points[1] shown on fig. 33, °C			
		Rotating feeder	Stationary feeder		25	24	23	26
Started both burners	7:35 a.m.	NAp	NAp	NAp	NAp	NAp	NAp	NAp
	9:00 a.m.	NAp	NAp	NAp	450	640	650	800
Started $TiCl_4$ feed	9:40 a.m.	15	1	0	600	765	740	920
	10:00 a.m.	15	1	52	575	755	740	860
	10:30 a.m.	15	1	143	500	775	740	770
	11:00 a.m.	15	1	244	510	785	740	730
Slowed feed rate	11:30 a.m.	12	1	261	530	795	740	730
	12:00 m.	12	1	451	560	775	735	735
Tapped 520 lb $MgCl_2$ at 820°C	12:35 p.m.	12	0	531	700	760	735	740
	1:00 p.m.	12	0	635	635	765	740	770
Slowed feed rate	1:15 p.m.	10	0	675	NM	NM	NM	NM
	1:30 p.m.	10	0	710	595	765	740	775
Broke light crust	2:05 p.m.	10	0	785	560	770	740	780
$TiCl_4$ feed off, stack damper partly closed	2:50 p.m.	0	0	886	570	765	740	775
Tapped 230 lb $MgCl_2$ at 860°C	3:00 p.m.	0	0	NAp	595	755	745	765
Tapped 50 lb $MgCl_2$	3:55 p.m.	0	0	NAp	720	750	745	765
Fire off, damper closed	4:05 p.m.	NAp	NAp	NAp	NAp	NAp	NAp	NAp

NAp Not applicable. NM Not measured.

[1] 25, chamber lid; 24, 14 in from chamber bottom; 23, 10 in from chamber bottom; 26, embedded in disk at chamber bottom.

no modification of the operating technique allowed the use of tetrachloride equivalent to more than 90 pct of the magnesium without introducing trivalent titanium into the slag.

The technique used for removing the mass of titanium sponge from the reaction chamber was admittedly rather cumbersome and expensive. Considerable effort was devoted to possible improvement, but without much success. One scheme tried was to use a thin sheet-iron liner inside the reaction chamber. After the reaction had been completed and the chamber had been cooled and opened, the liner containing the reaction mass was lifted out of the reaction chamber. The liner was peeled off the mass, and an attempt was made to crush the sponge mass in a jaw crusher to a particle size small enough for leaching. Stripping the liner was rather difficult and time consuming, and the reaction mass did not crush satisfactorily.

Some experiments were also conducted to determine whether greater care in preparing the raw materials would reduce the amounts of nitrogen and oxygen being carried into the titanium from these sources. Two drums of $TiCl_4$ were prepared under conditions such that the tetrachloride was protected by a helium atmosphere at all times during distillation, fractionation, and condensation, as well as during transfer from one vessel to another. Test compacts from lots of powder made from this feed material were not appreciably softer than usual. Therefore, it was concluded that the amount of oxygen and nitrogen dissolved in the tetrachloride was not great enough to justify the handling precautions.

The magnesium was normally loaded into the reaction chamber in the form of standard ingots, which had much more surface area and, therefore, more adsorbed gases than would a similar amount of magnesium in one large piece. To determine the significance of this factor, two runs were made using magnesium that had been remelted under helium into a single large cake. Although the product made from remelted magnesium had a slightly lower nitrogen content, no significant improvement was noted in the hardness of test compacts. It was concluded that the remelting of magnesium was not beneficial enough to justify the increased operating cost.

REFINING OF TITANIUM SPONGE

The mass remaining in the reaction chamber, after completion of the reduction of $TiCl_4$ with magnesium, is a mixture of titanium metal, magnesium metal, $MgCl_2$, and lower chlorides of titanium, together with minor amounts of contaminants from the process equipment, the magnesium, the tetrachloride, and the atmosphere. Separation of the major components was necessary to obtain titanium metal, and the separation procedures were a factor in controlling metal purity. In pilot-plant practice, approximately 80 pct of the $MgCl_2$ could be separated from the reaction mass by tapping while at the reaction temperature. After tapping, the reaction mass was 40 to 50 pct Ti, 45 to 55 pct $MgCl_2$, and 5 to 7.5 pct Mg.

In all of the small-scale experiments, separation of the reaction products was done by an acid leaching that removed the magnesium metal, MgCl, and part of the iron picked up from the processing equipment. Acid leaching was also used in refining the product obtained in the pilot plant. However, the leaching procedure added oxygen and hydrogen to the metal. While hydrogen was removed in vacuum sintering or melting, oxygen contributed more to the hardness of the metal than any other impurity element; therefore, a vacuum distillation refining process was developed to minimize oxygen pickup.

Refining by Leaching (*214*)

In the small-scale work, the leaching operation was conducted in glass laboratory equipment, and grinding was done in laboratory ball mills using iron containers and iron balls, which permitted magnetic separation of iron picked up in the grinding operation.

Figure 34 is a flowsheet for the leaching operation as practiced in the pilot plant. The acid leach was conducted in trunnion-mounted 50-gal glass-lined tanks equipped with cooling jackets. Agitation was provided by 400-r/min stirrers equipped with three-bladed Monel or stainless steel 8-in-diam impellers. The grinding unit was a 16- by 18-in ball mill with grate discharge operated in closed circuit with a 10- by 30-in vibrating screen. A 16-in basket centrifuge and drum dryer dewatered the second leach

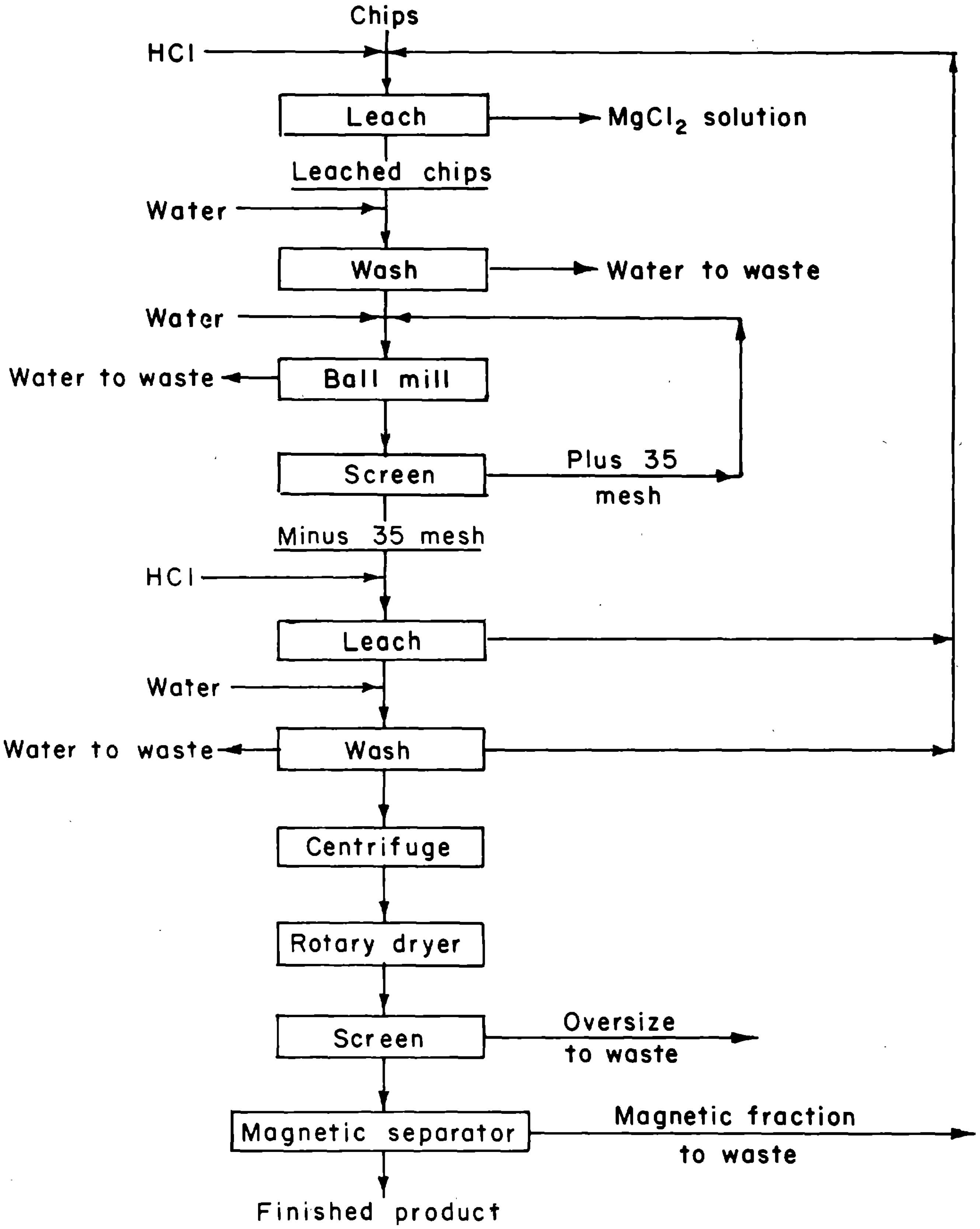

Figure 34.—Flowsheet of titanium chip leaching process.

powder product. A ring-type magnetic separator and a rotary drum blender (concrete mixer) were used in preparing composite lots for further research on physical properties.

Acid for the first leach was made up of acid and washings recovered from the second leach of the preceding batch. The pH of the leach solution was kept at 2 or lower to prevent formation of insoluble basic magnesium compounds. Such compounds coated the titanium particles and persisted through subsequent leaching, thus increasing the oxygen content of the product. Temperature during leaching was kept below 25° C to prevent formation of the basic compounds, and refrigerated brine was circulated through the cooling jacket during chip additions. The charge was allowed to stand overnight without further cooling or agitation, the $MgCl_2$ solution was decanted, and the sponge was given one wash with tap water and transferred to the ball mill.

The leached sponge was ground to minus 35 mesh. The pulp was elevated to the screen by a sand pump, and the oversize returned to the mill by gravity. The capacity of the mill varied according to the physical characteristics of the chips, ranging from 50 to 100 lb per 8-h shift.

The ground titanium powder was releached in 20° Be HCl diluted with an equal volume of wash water from the preceding centrifuge wash. During the second leach, it was not necessary to keep the temperature low as long as the powder was under vigorous agitation. Second leaches were conducted successfully at temperatures as high as 45° C. Higher temperatures selectively attacked the iron-titanium eutectic alloy present, reducing the iron content of the powder, sometimes by half. Higher temperatures had the disadvantage of increasing the hydrogen content of the product considerably.

After the period of agitation had been completed, the powder was allowed to settle, and the acid was decanted. Acid and wash were used for the first leach of the next batch. After one wash had been completed and decanted, the powder was loaded slowly into the centrifuge, washed with water until the washings were neutral, then washed once with distilled water, and centrifuged for 30 min. The dewatered powder was loaded into the drum dryer and dried in a current of dry air at room temperature. It was not desirable to use heat in drying, as moist titanium powder oxidizes rapidly when heated, even to 50° C.

The dried powder was passed through a 28-mesh sieve, and the undersize was passed twice through the magnetic separator to remove any free iron from the grinding balls or from turnings from the walls of the reaction pot. Magnetic separation was ineffective in removing that portion of the iron present as iron-titanium alloy because of its very low magnetic susceptibility. The oversize from the dry screening, consisting of a small amount of fuzz, chips, and other foreign material, was discarded. The nonmagnetic fraction from the separator was the finished product.

The various lots were analyzed and like lots were mixed to form composite lots of 500 lb, which were stored in sealed drums. The product for the 10 runs was recovered by leaching, and the finished powder represented an average recovery of 93.1 pct of the titanium fed to the leaching system.

Vacuum Distillation (35)

The purification of titanium chips from the reaction vessel by a leaching process had the disadvantage of increasing the nitrogen, oxygen, and hydrogen contents of the product. A vacuum distillation process had already been developed by the Bureau (*115*) for refining zirconium sponge produced by the Kroll process. An adaptation of this process was developed for the refining of titanium.

Equipment

Figure 35 is a sectional view of the distillation retort and heating jacket. The retort was a steel tube, 19 in ID and 78 in long. It was open at the bottom and sealed at the top with a reinforced steel head. The lower end was closed with a water-cooled removable base plate. The joint between the base plate and retort was sealed with a neoprene gasket and a fillet of vacuum wax.

The crude chips, contained in a mild steel basket, occupied the area at the top of the retort, and the lower portion served as the condenser. The lower section of the retort was surrounded by a cooling jacket, and the upper section was enclosed by the heating jacket. At a point 32 in above the bottom of the retort, a circular steel flange, 0.5 in thick and 48 in. in diam, was welded externally. Its purpose was to blank off the open end of the heating jacket when that unit was lowered over the retort. An annular water channel was welded to the bottom of the plate around its edge, and passing through the flange was a 2-in pipe nipple through which the heating jacket cavity could be evacuated.

The retort was evacuated through a 6-in outlet near its bottom. This outlet was connected by a gasketed, flanged joint to the vacuum manifold. In the latter, near the joint, an ionization-type vacuum gage was installed.

The equipment or "furniture" inside the retort, in ascending order, was as follows:

1. A 4-in-diam, 21-in-long pipe sealed at the top and welded to the upper surface of the base plate and cooled integrally with the bottom plate. The external surface of the pipe, the bottom plate, and the lower internal walls of the retort constituted the condenser.
2. Three sheet metal condenser shields covering the cooled retort walls, the 4-in pipe, and the baffle above the base plate. The shields were the actual condensing surfaces, and the condensate could be easily removed from the retort by removing the shields.
3. A 12-in-high spacer spider, consisting of a 3-in pipe with four radial fins resting on top of the condenser pipe and supporting item 4.
4. An 18-in-high spacer baffle, consisting of a section of 14-in pipe equipped internally with one or more dished baffles to reduce heat radiation to the condenser area.
5. A support grid, built up of steel plate sections 0.5 in thick and 2 in wide. Such a supporting device was necessary, as the bottom of the chip basket was too thin to support the 200-lb load at the operating temperature.
6. The cylindrical chip basket, constructed of 10-ga mild steel, which was perforated with 0.125-in holes on 0.5-in centers through which distillate escaped. Axially located within the chip basket was a length of 2-in steel tubing with 0.125-in walls that passed through the bottom and extended the length of the chip basket. It was perforated with 0.125-in holes to assist in the escape of distillate from the upper portions of the charge.

The heating jacket was cylindrical resistance-heated furnace that surrounded the upper portion of the retort. Welded to the top of the furnace shell was a 12-in-high cylinder to which were welded four radial reinforcing webs of 0.5-in steel plate, which supported the top when

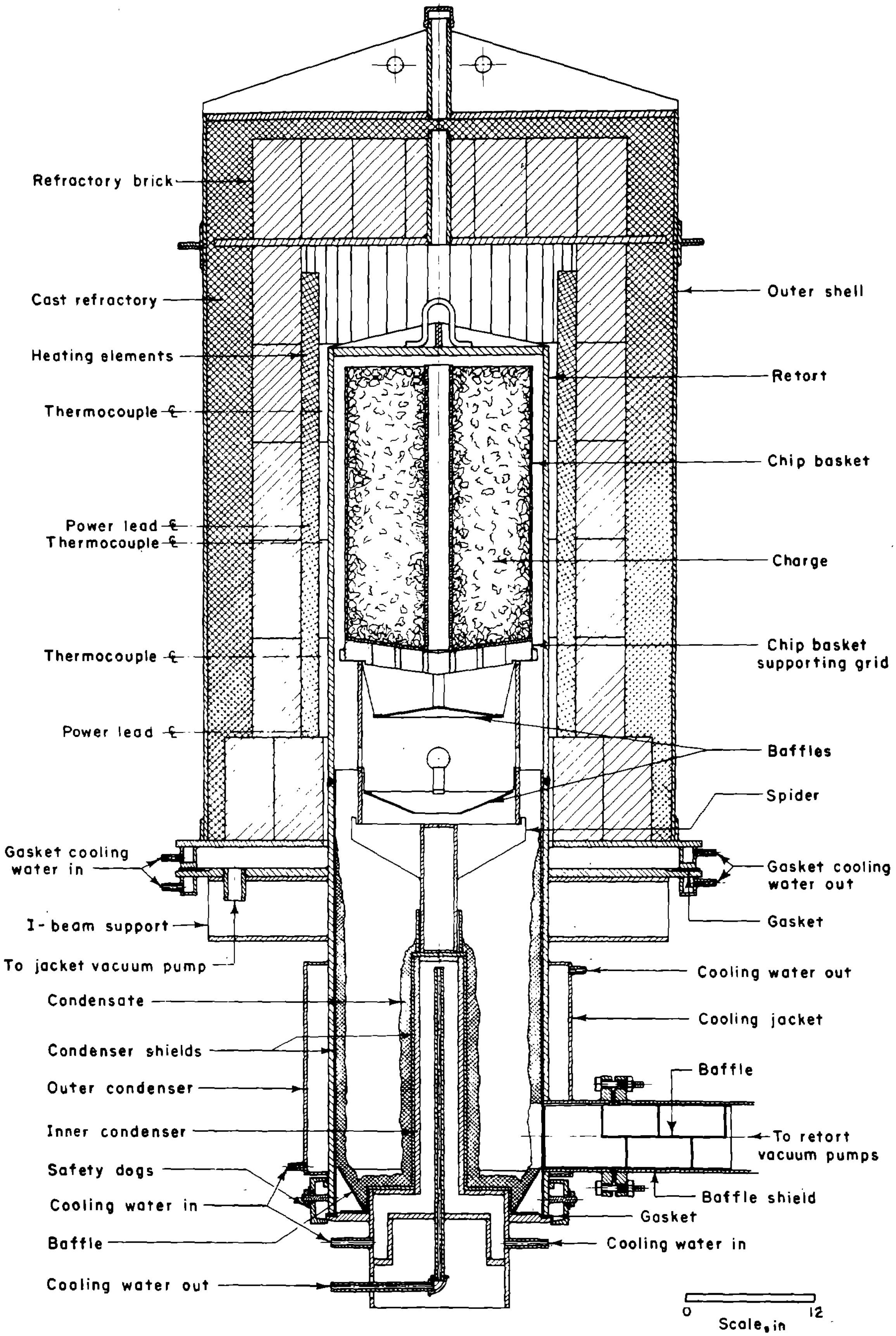

Figure 35.—Sectional view of distillation furnace.

the jacket was evacuated. To the lower end of the jacket was welded a 0.5-in-thick steel disk, 48 in. in diam, with a 22-in-diam hole in the center to accomodate the retort. Around the edge of the disk on the underside was a water channel that was a duplicate of that on the similar flange provided on the retort. A rubber gasket formed a vacuum-tight seal between the furnace flange and the retort flange.

The pumping system consisted of a two-stage oil-diffusion pump, backed by a single-stage mechanical pump. Contaminants, which were carried from the retort system to the mechanical pump over a period of time, were removed from the sealing oil in the pump by a unit that continuously circulated the pump oil through a filter.

Operating Procedure

Before loading the retort, all internal components were thoroughly cleaned. A portable elevator adapted from a forklift truck was used in loading the retort, the fork being replaced by a shelf on which the load was assembled. The loaded elevator was rolled into position under the furnace, and the assembly raised until the gasketed flange on the bottom plate bore against the lower edge of the retort, and the safety dogs were then engaged. A fillet of vacuum wax was placed around the gasketed joint, and the mechanical pump was started. After the retort pressure had dropped to about 20 in Hg, the elevator was removed. The loading operation was executed rapidly because of the avidly hygroscopic nature of the reaction mass chips. Moisture pickup was reduced by shielding the chip basket with a plastic cover that was placed over the basket in the dry room and removed as the charge was being elevated into the retort.

The diffusion pump was started when the mechanical pump had reduced the retort pressure to 1 mm Hg or less. A period of about 2 h was required for the pressure to reach equilibrium at about 0.1 to 0.3 µm Hg.

The heating jacket was then placed over the retort. Two retorts were served by one jacket; one retort was cooled, unloaded, and reloaded while the jacket was heating the other. The jacket was evacuated by connection through a valve to a vacuum manifold served by a 100-ft^3/min single-stage mechanical pump. Connections to the manifold existed at each retort, so that the one pump could evacuate the jacket regardless of which retort it was serving. Pumping for 30 min reduced the jacket pressure to less than 200 µm Hg, and the heating cycle was started. Evacuating the space between the heated section of the retort and the furnace shell served the dual purposes of protecting the outer surface of the retort from oxidation, while equalizing pressures inside and outside the retort to prevent its collapse at operating temperature.

A period of 3.5 to 4 h was required to bring the retort up to 925° C, the usual operating temperature. During heating, the rising temperature was accompanied by increasing pressure. Maximum pressure was attained shortly before the furnace reached operating temperature. The pressure rise was caused by evolution of gas adsorbed on the interior surfaces, by moisture, and, in the later stages, by hydrogen evolved from the titanium. In general, the maximum pressure was limited to the range between 1 and 2 µm Hg, and from this point, the pressure decreased slowly until at the conclusion of the run, the pressure returned to about 0.2 µm Hg. After 24 to 48 h at temperature, the furnace was allowed to cool. The retort was unloaded when it had cooled almost to room temperature. Data from a typical cycle are given in table 19.

To unload the retort, the elevator was positioned with the platform supporting the base plate, the safety dogs were removed, and helium was bled into the retort until atmospheric pressure was reached. This broke the seal, and the internal parts were lowered out of the retort and disassembled. The open end of the retort was then covered and remained covered until the next loading cycle. The use of helium to fill the evacuated retort minimized moisture pickup by the thin film of $MgCl_2$ always present on the retort walls. Besides adversely affecting the quality of the sponge, the moisture contamination would lengthen the pumpdown time required to reach the desired pressure for start of the next cycle.

Table 19.—Data for heating cycle in vacuum distillation purification[1]

Time, h	Temp, °C	Pressure, µm Hg			Remarks
		Forepump	Retort	Jacket	
0	[2]370	30	0.2	200	Power turned on.
1	620	80	2.0	150	
2	825	80	1.4	150	
3	925	60	.9	170	Up to temperature.
4	925	45	.45	160	
8	925	40	.3	130	
13	925	28	.3	130	
32	925	20	.3	130	Power turned off.
48	485	18	.2	100	Jacket removed.
72	30	25	.1	NAp	Unloaded (124 lb).

NAp Not applicable.

[1] Charge, 184 lb; loading time, 3 min; jacket evacuation, 45 min.

[2] Residual heat in jacket.

Immediately upon unloading the retort, the chip basket with its load of distilled sponge was removed to the dry room, where the sponge was removed from the basket, crushed to minus 0.5 in, sampled, and stored in sealed containers. During distillation, the separate pieces of sponge sintered together so that it was necessary to use a light pneumatic drill to dig out the sponge. The sponge removed ranged in size from powder to 4-in lumps. The larger pieces were reduced to minus 0.5 in. in a small jaw crusher, while the finer material was fed to a 12- by 30-in trommel covered with 0.5-in-mesh screen. The crusher product was also screened, and the oversize from both sources was passed through the crusher several times. After each pass, the crusher opening was reduced, so that after several passes, the entire mass had been reduced to the desired size. After crushing, the product was sampled using a Jones splitter.

Experimental Results

The extent of which magnesium and $MgCl_2$ were removed from the charge was found to be primarily a function of the time and temperature of treatment. Variation of pressure in the retort, within the range investigated, did not affect the efficiency of the distillation.

Heating times of less than 18 to 20 h at 925° C gave erratic results. A heating time of 24 h was convenient, as only day-shift labor was required. Table 20 lists data from distillation runs with 24- to 30-h heating times and table 21 lists similar data for 48-h runs. There was no consistent difference in the removal of magnesium or chlorine for the different distillation times, indicating that the 24-h heating cycle represented a near optimum for distillation efficiency. There was a wide variation in ratio of weight of chips to distillation products in the various runs, but this

Table 20.—Operating data, 24- to 30-h heats, 10 runs

	1	2	3	4	5	6	7	8	9	10	Average
Chips charged . . . . lb . .	176	140	166	204	198	181	229	200	189	207	189
Ti sponge produced . . . . lb . .	114	93	110	121	130	115	131	135	120	126	119.5
Mg and $MgCl_2$ distilled . . . . . lb . .	62	47	56	83	68	66	98	65	69	81	69.5
Mg-$MgCl_2$ ratio	1.82	1.98	1.80	1.46	1.91	1.76	1.32	2.08	1.74	1.56	1.74
Time at temperature . . . . h . .	24	26.5	24	27	24	26	24	27	32	30	
Energy, kW·h:											
Total[1]	1,362	1,487	1,362	1,512	1,362	1,462	1,362	1,512	1,762	1,662	1,485
Per pound of sponge	12	16	12.4	12.5	10.5	12.7	10.4	11.2	14.7	13.2	12.6
Mg in sponge . . . . pct.	0.07	0.02	0.02	0.04	0.036	0.045	0.035	0.024	0.033	0.023	0.035
Cl_2 in sponge . . . . pct.	0.07	0.06	0.07	0.09	0.07	0.08	0.08	0.06	0.075	0.075	0.073

[1] Includes consumption during 3.25-h furnace preheat period.

Table 21.—Operating data, 48-h heats, 10 runs

	1	2	3	4	5	6	7	8	9	10	Average
Chips charged . . . . lb . .	205	175	201	176	198	199	198	203	195	199	194.9
Ti sponge produced . . . . lb . .	133	100	132	117	95	119	137	130	122	136	122.1
Mg and $MgCl_2$ distilled . . . . lb . .	72	75	69	59	103	80	61	73	73	63	72.8
Mg-$MgCl_2$ ratio	1.85	1.33	1.91	1.98	0.93	1.49	2.05	1.78	1.68	2.15	1.71
Time at temperature . . . . h . .	49.5	47.5	49	48.5	47.5	48	48	48.5	47.5	47.5	48.2
Energy, kW·h:											
Total[1]	2,637	2,537	2,612	2,587	2,537	2,562	2,562	2,587	2,537	2,537	2,570
Per pound of sponge	19.8	25.4	19.8	22.1	26.7	21.5	18.7	19.9	20.8	18.7	21.3
Mg in sponge . . . . pct. .	0.045	0.036	0.04	0.045	0.027	0.032	0.038	0.032	0.023	0.022	0.034
Cl_2 in sponge . . . . pct. .	0.06	0.055	0.07	0.075	0.055	0.06	0.085	0.08	0.06	0.08	0.068

[1] Includes consumption during 3.25-h furnace preheat period.

was not reflected in distillation efficiency in either the 24- or 48-h runs. The variation in $MgCl_2$-Ti ratio in the charge resulted from the reduction and chip recovery steps. Varying amounts of $MgCl_2$ could be tapped from the reduction reactor in different runs, and in addition, chips bored from different zones of the reactor contained varying proportions of $MgCl_2$.

Double distillation, comprising two separate distillations for 24 h each at 925° C, was more effective than one 48-h distillation. Table 22 shows that the magnesium content could be reduced to 0.02 pct by this procedure. The sponge was removed from the chip basket, crushed, and sized between distillatiions. This procedure evidently opened new paths for magnesium and $MgCl_2$ to escape during the second distillation.

Table 22.—Analyses comparison of identical lots of sponge after two 24-h distillations, weight percent

Sponge	Mg	Cl_2	N_2	Fe
Lot 1032:				
1st 24-h distillation	0.040	0.075	0.009	0.045
2d 24-h distillation	.019	.059	.009	.055
Change	−.021	−.016	0	+.010
Lot 1033:				
1st 24-h distillation	.045	.085	.009	.030
2d 24-h distillation	.020	.050	.009	.043
Change	−.025	−.035	0	+.013

The temperature at which the distillation was conducted had a marked effect on distillation efficiency. A reduction of 30° C in the distillation temperature resulted in an average 8-pct increase in the magnesium content of the product, even when the distillation time was doubled for the lower temperature runs. This indicated that higher temperatures would be advantageous; however, the use of higher temperatures resulted in formation of the iron-titanium eutectic alloy with the iron equipment at indicated temperatures above 925° C. In distilling zirconium sponge at the Bureau in Albany, OR, it was found that higher temperatures could be used without iron contamination if the sponge container was constructed of a 12-pct chromium-iron alloy. It is probable that this would also hold true for titanium.

No significant effect was observed from pressure variation within the range investigated. It was noted that there was no important difference in the quality of the sponge produced with an end pressure in the retort of 0.2 µm Hg and that produced with an end pressure of 0.02 µm Hg. This variable was further investigated in a run without the diffusion pump, the mechanical pump alone being used throughout the run. The pressure ranged from a peak of 140 µm Hg as the charge was heated to an end pressure of 17 µm Hg several hours before the end of the run. Time of treatment was 47.5 h and the temperature was 925° C. The magnesium content of the product was not higher than for regular runs.

One further step was taken in pursuit of this line of investigation. In this experiment also, the diffusion pump was not used. The furnace was heated to 925° C, and when the pressure within the retort had reached equilibrium after 22.5 h, the system was sealed by closing the valve in the line to the vacuum pump. The valve remained closed for the balance of the 48-h run, but significantly, only a minor rise in pressure ensued, undoubtedly because of the gettering effect of the titanium and magnesium. Product quality was not adversely affected.

The vacuum distillation purification system was further developed in a 1,500-lb/d demonstration plant described later in this report.

Comparison of Refining Processes

Each of the refining processes investigated, leaching and vacuum distillation, had its advantages and drawbacks.

The leaching procedure could be adapted to continuous operation, and equipment was less costly, longer lived, and obtainable as standard items from manufacturers. Leaching also offered opportunity for reduction of some impurities, such as iron, by solution and by magnetic separation. Titanium powder, then thought to be adaptable for powder metallurgy applications, was more easily produced from the leach product than from chips produced in vacuum distillation. The major disadvantage of leaching was the increase in oxygen and hydrogen contents of the product and increased difficulty in arc melting because of the higher content of magnesium and $MgCl_2$.

Vacuum distillation resulted in a product with lower oxygen, hydrogen, nitrogen, magnesium, and magnesium chloride contents than could be obtained from comparable crude chips by leaching. Disadvantages were that it was a batch operation, special materials of construction were required, pressure-temperature requirements limited the size of distillation units, equipment required protection from atmospheric moisture to prevent oxygen contamination, and the equipment and maintenance costs were higher than for the leaching procedure.

CHAPTER 4.—DEMONSTRATION-PLANT OPERATION (*13*)

The titanium sponge produced in the previously described Bureau pilot plants and additional sponge produced on a small scale by industrial companies were used in determining the physical properties of titanium metal, in development of processing and fabricating techniques, and in construction of prototype equipment (*37-38*). These developments demonstrated that titanium had unique properties that would lead to its use in many applications. Cost considerations were a major factor in evaluation of potential applications. The military services were particularly interested in developing a low-cost production process. In 1952, the Ordnance Corps, Department of the Army, provided the Bureau with funds to erect a plant with a titanium sponge production capacity of 1,500 lb/d. The plant was intended to effect process improvements and to develop a continuous process. During construction of the plant, Bureau research on continuous processes showed that the magnesium reduction process was difficult, if not impossible, to adapt to continuous operation. A summary of the research on continuous operation procedures is given in chapter 5.

Operations in the 1,500-lb/d plant were started on an intermittent basis in July 1952 with a batch reduction technique similar to that developed in the pilot plant. Primary objectives were to test the equipment and to develop a standardized operating procedure.

In 1953, the Defense Materials Procurement Agency (DMPA) negotiated a contract with the Bureau for production of a minimum of 360,000 and a maximum of 500,000 lb of ductile titanium. Although evaluating techniques of production for military applications became the main objective of plant operation, an opportunity was also provided for further investigation of many problems that could be evaluated only in a large, continuously operating plant. In addition, prospective industrial producers could view an operating plant and study firsthand some of the new metallurgical techniques involved, such as high-temperature inert atmosphere and vacuum distillation operations. Operation under the DMPA contract resulted in production of 492,503 lb of acceptable metal. The hardness of buttons arc-melted from the sponge averaged 152 HB. Twenty-five percent of the batches were 140 HB or under, 70 pct were between 141 and 180 HB, and 5 pct were over 180 HB.

After conclusion of the production for DMPA, the Bureau entered in a cooperative agreement with the Wah Chang Corporation to conduct further research and development in the demonstration plant to improve the quality of the sponge produced. Under the agreement, 220,611 lb of sponge with an average hardness of 114 HB was produced. Under optimum conditions, batches were produced with hardnesses below 110 HB and as low as 90 HB.

The production scheme used in the demonstration plant was essentially a scaleup of that developed in the pilot plant. A flowsheet of the process is shown in figure 36. Sponge refining was accomplished by a modified distillation procedure.

BUILDING AND GENERAL LAYOUT

The general floor plan of the demonstration plant housed in a 72- by 102-ft building, is shown in figure 37.

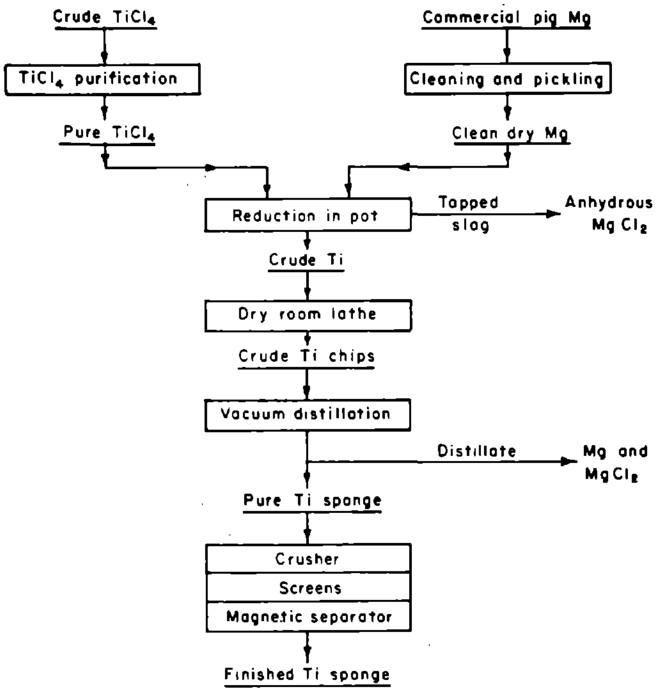

Figure 36.—Titanium production flowsheet.

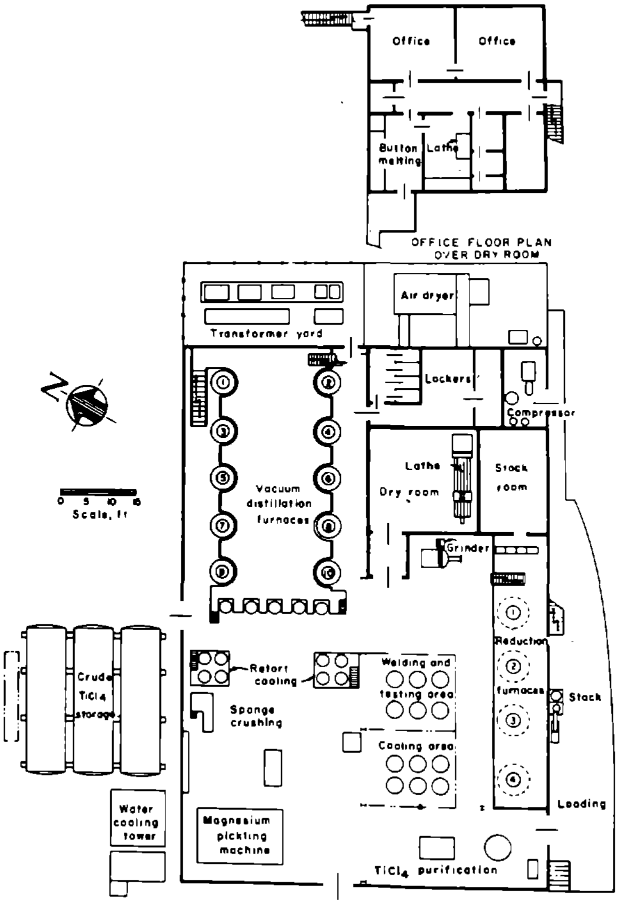

Figure 37.—General floorplan of titanium plant.

There was a concrete loading dock at the south side of the building, adjacent to a rail spur. An 18- by 72-ft concrete slab at the east end of the building held the transformer yard and an automatic air dryer for the dry room. A partial second floor, about 36 by 36 ft, housed two offices and a control laboratory.

REDUCTION OF TITANIUM TETRACHLORIDE

Reduction Equipment

The purified $TiCl_4$ was reduced in mild steel reactor vessels or pots. Various modifications were tried, and a dimensioned outline drawing of one of the best designs is shown in figure 38. A cross section of this reactor and the furnace in which it was heated are shown in figure 39.

The pot was made up of two parts; the lower container, and the lid, which carried a top column. The top column provided for the following: (1) inlet for $TiCl_4$, (2) gas bleed-off outlet to adjust internal pressure, (3) helium inlet, (4) manometer connection, and (5) thermocouple tube through which the internal temperature could be sensed. Additional features were (1) a tapping spout at the bottom of the pot to permit drainage of $MgCl_2$, (2) thermocouple wells on the sides of the pot for temperature control, (3) lugs and hooks to handle the pot and to attach the pot to the lathe to remove chips, (4) a suitable arrangement of flanges to permit welding the lid to the pot, and (5) a means for air cooling the column.

The plant had four reduction furnaces, each provided with automatic temperature recorders and controllers. Each furnace was heated by two gas burners and had suitable openings for thermocouples, cooling ports, a slag launder, and gas-exhaust ports. A third portable auxiliary burner was provided for heating the tapping spout before tapping $MgCl_2$. A steel operating floor 7⅓ ft above the ground floor provided access to the top of the pot columns.

Each reduction pot was fed from a 120-gal feed tank located in the $TiCl_4$ purification bay. A water-cooled plug was pressed against the taphole opening of the pot and held tightly in place by a spring. Slag launders were made from 5-in-diameter mild steel pipe and had an overall length of 46.5 in. A slit opening, 3.5 in wide and 42 in long, was cut into the top to provide room for opening and closing the taphole.

A 100-ft^3/min single-stage vacuum pump was used to evacuate the pots. The hookup included piping and valving necessary for exhausting several pots at one time.

Preparation of Magnesium

The magnesium used was required to meet ASTM specification B-92-45. Ingots weighed approximately 20 lb each and analyzed not less than 99.8 pct Mg. The sum of aluminum, copper, iron, manganese, nickel, and silicon contents could not be over 0.2 pct. The copper content was to be less than 0.02 pct and the nickel less than 0.001 pct. All magnesium ingots were pickled in dilute HCl to a uniformly bright and clean surface, followed by thorough washing and drying.

Reduction Operating Procedure

The reactor pots were loaded in the dry room with approximately 330 lb of magnesium ingots, and the lid

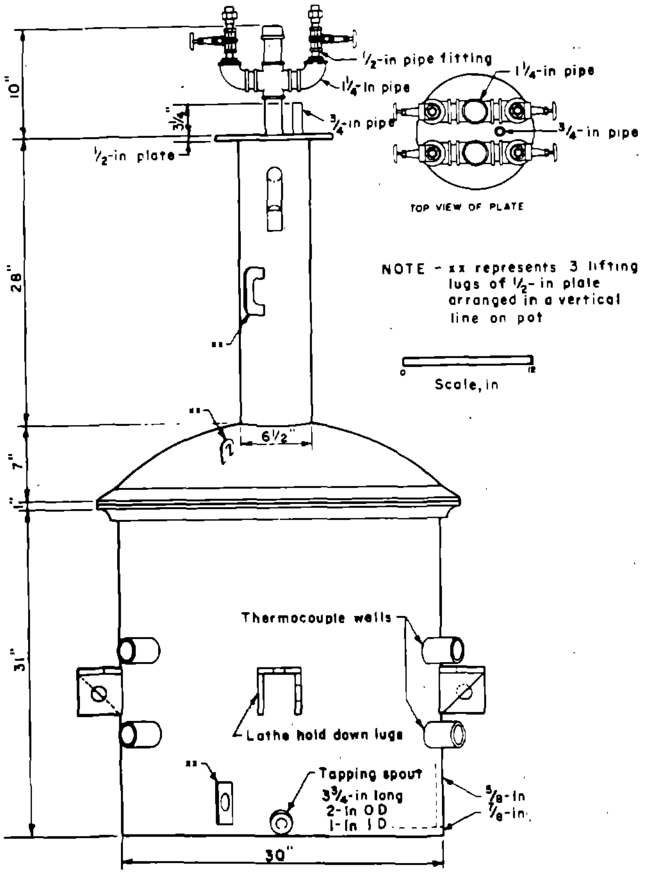

Figure 38.—Elevation of reduction pot.

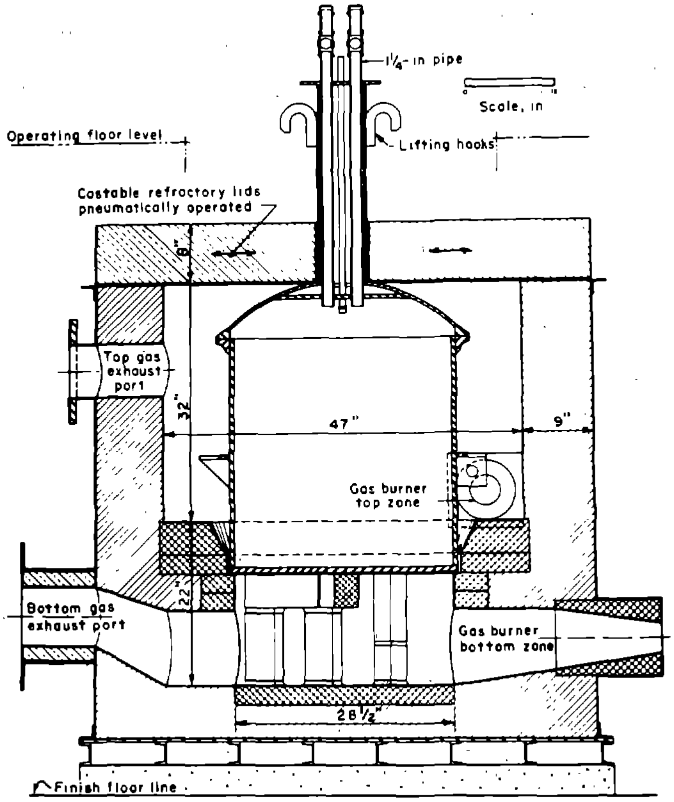

Figure 39.—Cross section of reduction pot and furnace.

was welded to the pot by running a bead around the joint between the lid and the pot. A tight weld with only slight penetration was obtained, which required minimum grinding when the weld was removed. After leak checking and stopping all the apparent leaks, the pot was weighed and evacuated to approximately 27 in Hg. If the vacuum dropped more than 1 in Hg in 20 min, the pot was retested for leaks and the leaks stopped. When vacuum was maintained, the pot was filled with helium, reevacuated and repurged twice to assure elimination of as much air as possible before heating. The pots were then ready to be placed in the furnace.

After the pot was placed in the furnace and all lines and thermocouples were connected, the burners were started and the controller set at 750° C. Helium was fed into the pot at a low rate until it bubbled slowly through the bubbler, and flow was maintained during the heating cycle so that any moisture could be driven out. Before beginning to feed $TiCl_4$, the bubbler was disconnected and the bubbler line was connected to the manometer. After this, a helium pressure of about 0.5 in Hg was maintained in the pot. About 1.5 h usually elapsed before some of the magnesium melted and $TiCl_4$ feed was started.

The feed was initially adjusted to a low rate of about 30 lb/h because there was a 5- to 20-min time lag before the reaction began, and this tended to cause a pressure rise in the pot from $TiCl_4$ vapor. Attempts were made to keep the pressure at 0.5 lbf/in^2(ga) or 1 in on the mercury manometer. When the pressure increased above this point, $TiCl_4$ vapor had to be vented, and lower pressures required the addition of helium.

The start of the reaction was indicated by a pressure drop, and the feed rate was gradually increased up to 200 to 250 lb/h. This rate of feed was determined experimentally to produce the most consistent quality of titanium sponge. The furnace burners were shut off when the rate of reaction generated enough heat to maintain the desired temperature of 750° to 800° C. The reaction supplied the required heat for approximately two-thirds of the reduction cycle. The lower burner was left on automatic control, set at about 740° C, so that the bottom of the pot would not drop below the solidification temperature of $MgCl_2$. If the temperature started to rise or drop rapidly, the feed rate was adjusted until the temperature remained fairly constant.

About 2 h after starting addition of feed, approximately 40 pct of the $TiCl_4$ had been added, and the first tapping of $MgCl_2$ was made. The feed rate was usually reduced to about 180 lb/h after the first tapping to prevent a pressure increase and the formation of lower chlorides of titanium caused by the presence of excess $TiCl_4$. Magnesium chloride was again tapped when 60 and 100 pct of the feed had been added.

In practice, the cycle of operations could not be held to an exact schedule because difficulties were encountered in feed rates, temperature control in different zones of the reactor, tapping of the $MgCl_2$, and obstruction of feed and vent lines. These factors caused undesirable side reactions and delays in the schedule, and often led to possible infiltration of air into the reactor. Crusts of $MgCl_2$ that formed during some runs prevented contact of the reacting materials and resulted in an increase in pressure that persisted in spite of a reduction in feed rate. To promote an increase in reaction rate, this crust was broken by poking with a clean, dry steel rod that was inserted quickly through one of the 1.25-in-diam pipe inlets. When poking was necessary, it was usually near the end of the run when the availability of magnesium was diminished considerably. By keeping the pot lid about 200° C cooler than the pot body, the necessity for poking was minimized.

After all of the $TiCl_4$ had been added, the burners were again turned on, and the temperature of the reduction pot at the controller point was held at 780° to 850° C for 1 h. This heating period allowed further drainage of $MgCl_2$ from the reaction mass and also made entrapped magnesium available for reaction with any unreacted tetrachloride or lower chlorides. A final tapping was made to remove as much $MgCl_2$ as possible from the pot.

The pot was cooled in the furnace for 1 h to prevent warpage and then was removed from the furnace and set on brick piers to continue cooling. The inside of the pot was kept under 0.5 to 1 lbf/in^2(ga) of helium during the cooling period. When room temperature was reached, the pot and its contents were transferred to the swing-frame grinder where the weld was ground off. Grinding was continued until a fine crack appeared on the flange, then C-clamps were used to hold the lid to the body, and the pot was transferred to the dry room where the lid was removed.

Recovery of Crude Titanium Sponge

At the end of a production run, the reactor pot was nearly filled with a solid mass of titanium sponge intermixed with anhydrous $MgCl_2$ and unreacted magnesium. Because it was extremely important that the crude titanium mass be protected from accumulating water of hydration, the reactor pot was opened in a dry room. The contents were turned out on a lathe into chip baskets which went to the distillation retorts for vacuum distillation of the magnesium and $MgCl_2$. The empty reactor pots were refilled with magnesium ingots, and the lids were clamped on tightly and taped before the pots were sent to the welder.

Dry-Room Equipment

The dry room was an insulated airtight room. An entrance vestibule with inner and outer steel weatherstripped doors served as an airlock for entry and exit. During operations, the inner and outer doors were never opened at the same time.

A commercial air dryer utilizing activated alumina as the moisture absorbent supplied dried air to maintain a dewpoint of -15° to -45° F in the room.

To assure minimum exposure of the titanium sponge chips to air as they were removed from the pot, a removable hood was installed over the lathe head and boring tool. A "lance" of 0.25-in-diam pipe, through which helium could be supplied to the cutting area, was directed at the cutting edge of the tool. Inert gas was directed to this area whenever danger of fire appeared imminent during turning.

Dry-Room Operations

Immediately after the lid was removed from the pot in the dry room, a plywood cover that had a 0.5-in opening in the center for a helium line was placed on the pot. When a fire started, the helium was turned on and an inert gas blanket was maintained over the reaction mass until the fire was smothered. An opened reactor with its reduction mass is shown in figure 40.

Figure 40.—Reduction pot with lid removed, showing reduction mass.

The pot was securely fastened in the lathe by four long bolts, which fitted into slots in the lathe faceplate and extended to brackets welded to the pot. The adjustable jaws were tightened to center the pot, and the hood was lowered into place and bolted down.

Most pots were turned out at 32.5 r/min with a 0.5- to 0.75-in cut and a crossfeed of 0.232 in per revolution. When hard sponge was encountered, speeds and feeds were reduced. The average elapsed time for turning out a pot was 105 min. Figure 41 shows the complete assembly in operation. A 0.75-in shell of reaction products, which had a relatively high iron content, was left on the sides and bottom of the pot to reduce iron contamination of the chips. For all practical purposes, the pots were lined with crude titanium sponge after the initial run. Buildup on the inside of the lid was removed, and any metal, usually found in small fragments, was placed in the chip basket.

After a pot was emptied, the hood was removed, the pot was taken from the lathe, immediately filled with a new weighted charge of magnesium, and the lid was set in place. The chip basket was removed from the pit under the lathe and placed in a tightly closed storage can until the distillation schedule was ready for it.

Refining of Crude Sponge

Distillation Equipment

Refining was accomplished by vacuum distillation. The equipment used was similar to that described in connection with pilot-plant operations except that the major sections, distillation and condensation, were interchanged. The furnace and charge were the lower section, and the top was the condenser. There were 10 distillation stations as shown in figure 37. The furnaces were arranged in two rows of five each on the ground floor and were surmounted by an operating deck provided with circular openings above each furnace for loading the retorts. Figure 42 shows five retorts mounted in cradle racks in front of the operating deck, a sixth retort in a cooling rack at the right foreground, and 10 distillations in progress in the background. Figure 43 is a cross-sectional view of a furnace with a retort in place.

The retort consisted of a 96- to 99-in-long, 27-in-ID tube closed at the bottom. Welded to the side of the retort about 60 in from the bottom was a flange for supporting the retort on the furnace at operating deck level. Another

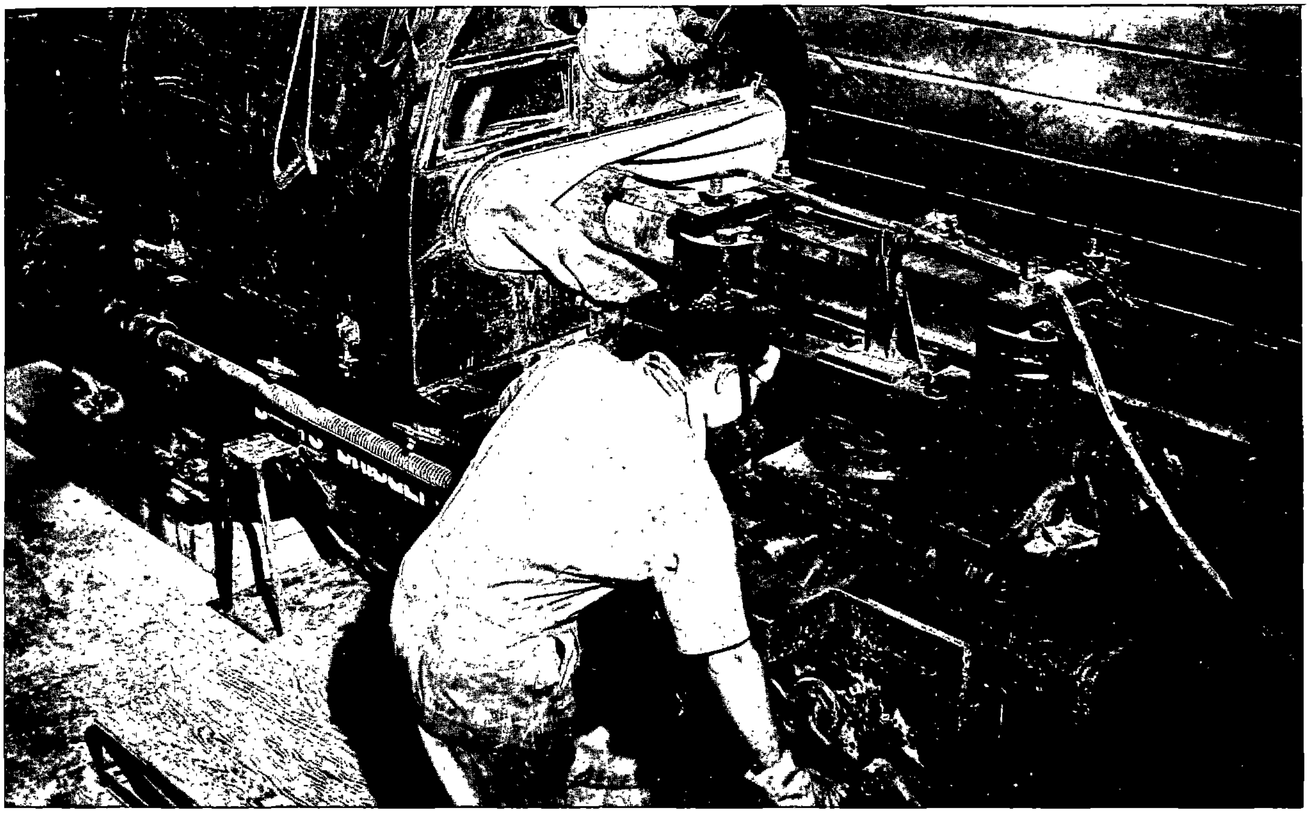

Figure 41.—Lathe hooded and turning out crude titanium chips from reduction pot.

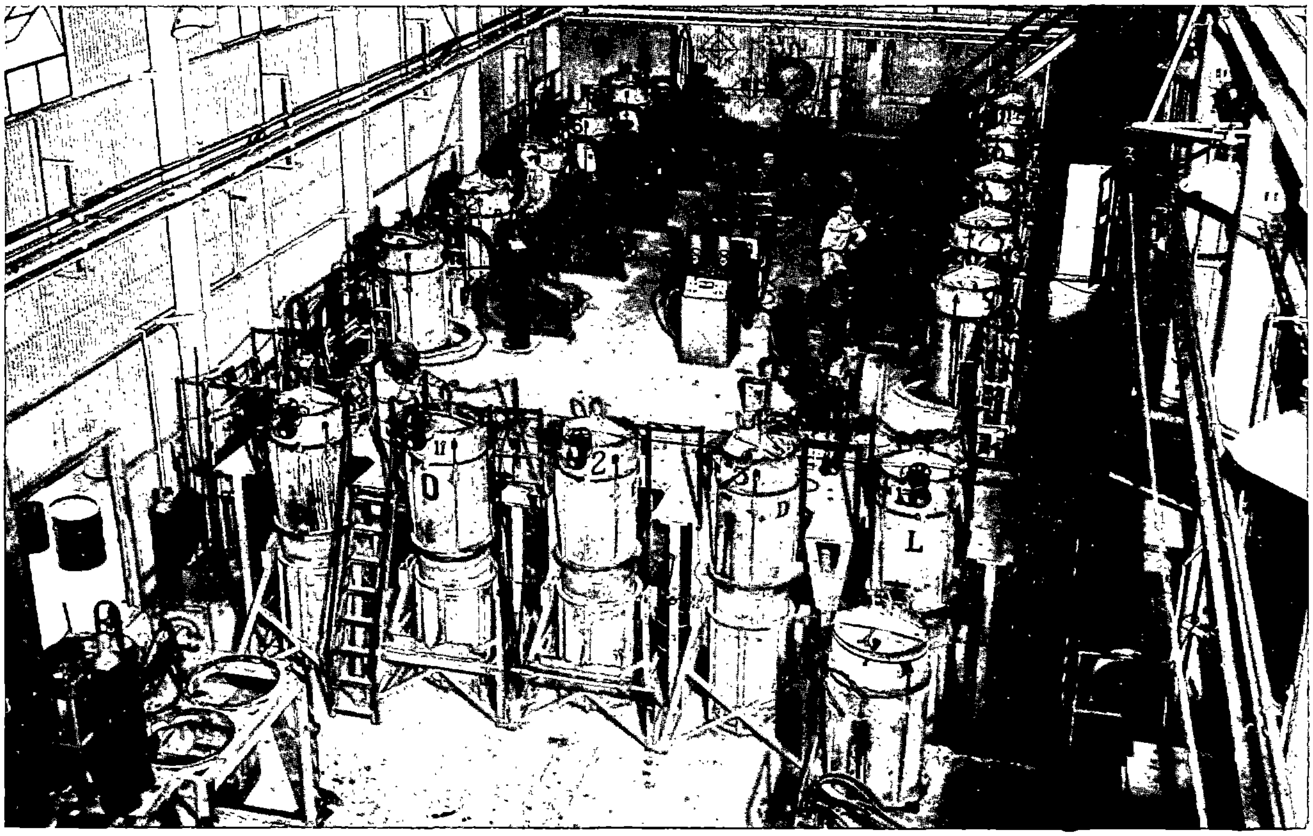

Figure 42.—General view of vacuum distillation area.

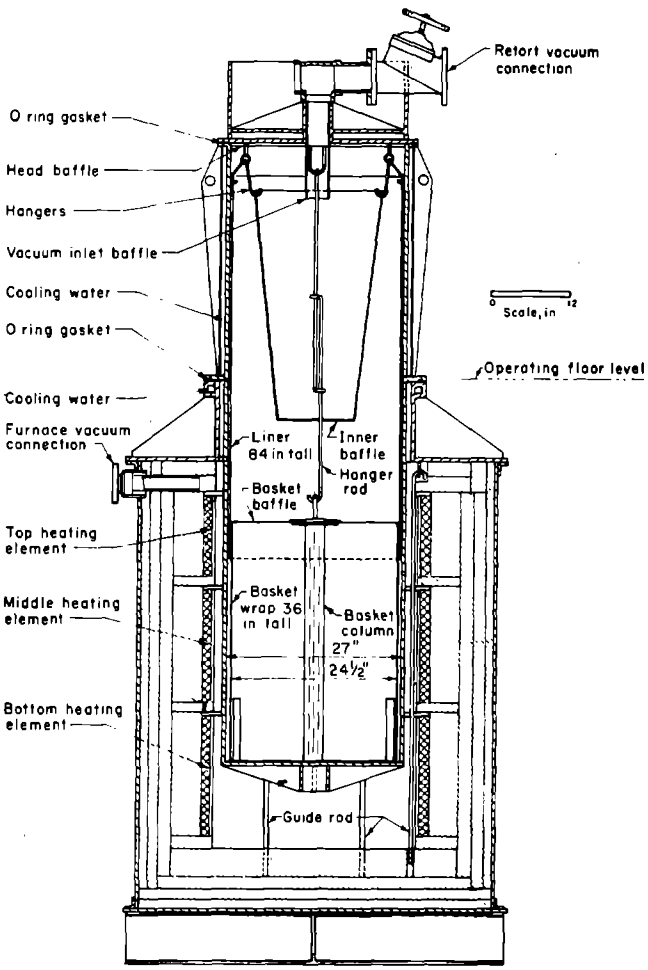

Figure 43.—Cross section of vacuum furnace and distillation retort.

flange was located at the top of the retort tube for the retort cover. Both of these flanges were machined to make vacuum-tight seals against O-ring gaskets set in shallow grooves. The weight of the retort was sufficient to maintain the seal between retort and furnace, but the retort cover was secured to the retort by four permanently attached bolts and holddown lugs spaced evenly around the retort and cover.

The retort was of 0.5-in-thick mild steel, and the bottom portion was metallized on the outside to guard against oxidation at operating temperature. The condensation area of the retort was water jacketed for cooling. A 3-in outlet in the center of the cover was fitted with a vacuum valve, which was connected to the vacuum pump with a rubber hose. A valved 0.375-in line was connected with rubber tubing to a Hastings vacuum-gauge tube. The cover was provided with a water jacket. The underside of the cover had two threaded studs and four eyebolts for carrying the retort furniture and a 0.5-in U-bolt at the center from which the chip basket was hung.

During distillation, the loaded chip basket was at the bottom of the retort, and a number of baffles, known collectively as retort furniture, occupied the upper part of the retort. The furniture provided a large area in the cold part of the retort for the impingement and condensation of the magnesium and $MgCl_2$ vapors to minimize carryover of condensable material into the vacuum lines and pumps.

Each retort was provided with a separate single-stage, rotary, oil-sealed pump with a theoretical displacement of 100 ft^3/min of free air and capable of producing a vacuum of 5 µm Hg on a blank flange test. An additional pump was used for outgassing and preliminary evacuation of retorts. No booster or diffusion pumps were used.

The furnaces were open-topped, circular, electrically heated pot furnaces, 91 in high, 60 in. in diameter, and 72 in deep from the flanged top opening. The furnaces were gas tight and designed to withstand a vacuum. The heating zone was 48 in high and was divided into three heating zones, each with a separate power supply. The heating elements were protected by vertical guides or skids to prevent damage when the retort was lowered into the furnace. Each furnace had two thermocouples in each heating zone. One of each pair was connected to a controller, the second was connected to an emergency, high-limit controller.

The furnaces were evacuated through a 5-in manifold header that connected to each furnace through a 2-in line controlled by a diaphragm valve. The furnace vacuum pump was similar to those used for retort evacuation except that capacity was approximately 300 ft^3/min of free air.

The entire distillation area was served by a 5-st-capacity overhead traveling crane.

Operating Procedure

To begin a distillation cycle, the retort head was removed from the retort and left suspended on the crane about 5 ft above floor level. The retort furniture was then assembled and attached to the retort head. When the assembled retort furniture was raised about 5 ft above the floor, the lower end of the telescope hook hung below the furniture. The loaded chip basket was then quickly wheeled out of the dry room, still in the storage can to protect the titanium chips from the atmosphere, and fastened to the telescope hook below the furniture. The entire assembly was raised free of the storage can and lowered into the retort, as shown in figure 44. The retort was then sealed and connected to a vacuum pump for preliminary evacuation. Normally, the loaded chip basket was exposed to undried air for only 1 to 2 min after leaving the dry room.

Preliminary evacuation, performed by the auxiliary pump, was continued for about 4 h to outgas the retort and its contents. The vacuum had to be less than 200 µm Hg before the retort was considered ready for the furnace. After the retort was placed in the furnace, cooling water and vacuum lines were connected, the vacuum pumps were started, and valves in the vacuum lines to the retort and the furnace were opened. When the pressure in the retort had dropped below 75 µm Hg, furnace power was turned on. Vacuum in the space between the furnace shell and the outside of the heated portion of the retort was maintained above about 27 in Hg.

High distillation temperature was the most effective means of lowering the residual magnesium and chloride content of the sponge, but temperatures above about 940° C caused distortion and elongation of the retorts. The quantity and composition of each charge depended mainly on the efficiency of the reduction and the amount of magnesium and $MgCl_2$ left in the crude sponge. Every effort was made to remove as much $MgCl_2$ as possible in the last tapping after reduction was completed, but the amount of residuals that had to be distilled varied

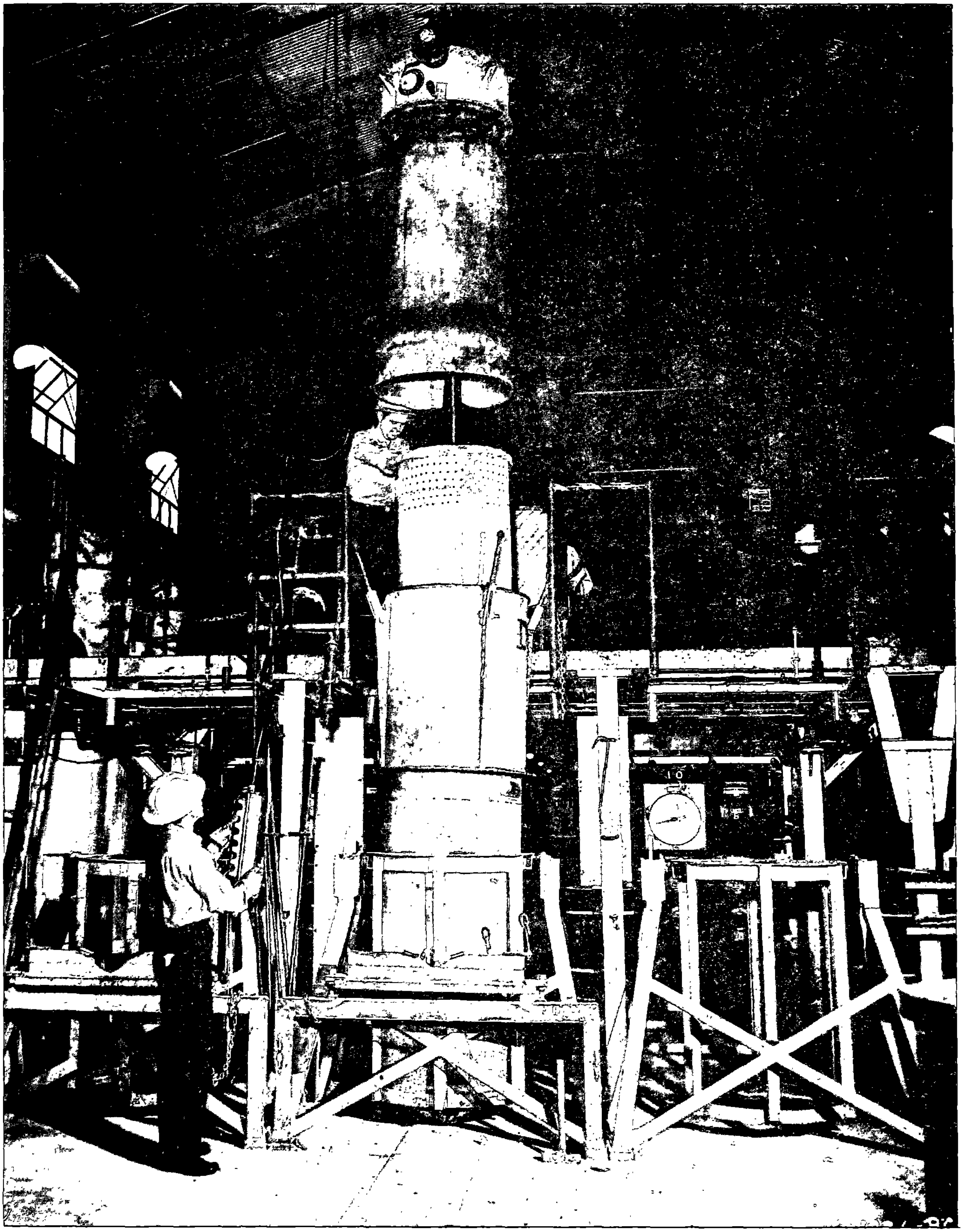

Figure 44.—Loading a retort, showing loaded chip basket entering the retort from above.

Table 23.—Typical weights of chips and sponge, runs 2050 through 2149

	Weight, lb		Quantity distilled	
	Chips	Sponge	lb	pct
Heaviest charge	563	323	240	42.6
Lightest charge	300	181	119	39.7
Average	429	256	173	40.3

considerably from run to run. Also, the quantity of chips recovered during the lathe turning varied appreciably, depending on the thickness of the lining left in the pot. Table 23 lists the extreme and average weights of chips and the resulting titanium sponge from 100 runs selected at random from the plant operations. All of these runs started with virtually the same charge of magnesium. Although the extremes showed a large variation, most of the batches were close to the average.

Time was the factor that could be most easily varied from a practical standpoint. Abnormally long distillation times proved to be of little benefit, but insufficient time or temperature produced sponge metal containing excessive residual magnesium and chloride. Such batches had to be redistilled.

Redistillation always resulted in much harder sponge because moisture was picked up during unloading, crushing, and reloading. Redistillation also interrupted the established production schedule and could be avoided by using a long distillation cycle. Much experimentation was conducted to determine optimum conditions for the particular equipment in the plant. Cycles as long as 82 h at 882° C and as short as 22 h were used experimentally. One of the best cycles was to maintain the retort at a temperature of 940° C for 31 h. The 10 furnaces had a maximum capacity of about 1,600 lb/d of finished sponge with batches averaging 260 lb each.

In the early stages of distillation, the process of vaporization and condensation of magnesium and $MgCl_2$ was comparable to the action of a diffusion pump. When most of the magnesium and $MgCl_2$ had been removed, the gettering action of the hot titanium caused a vacuum to develop in the retort that exceeded the vacuum capacity of the mechanical pump. This transition usually occurred after 16 to 20 h at distillation temperature. The valve in the line to the vacuum pump was then closed to prevent contamination of the titanium in the retort by the backflow of oil vapor from the pump. The exact time for closing the valve was determined by comparing the vacuum in the retort with that at the pump. This practice prevented carbon deposits in the condensing zone of the retort and avoided hydrocarbon contamination of the titanium by vacuum pump oil.

At the end of the distillation cycle, the furnace was turned off and allowed to cool to below 870° C. A helium line was then connected to the retort, the 2-in valve in the vacuum line to the furnace was closed, and the retort and furnace cavities were filled with helium and dry air, respectively. A positive pressure of about 1.5 lbf/in^2(ga) of helium was left in the retort when it was removed to the cooling rack. At the cooling rack, helium and cooling water lines were reconnected and helium pressure and water flow were maintained throughout the remainder of the cooling period.

After 22 h in the cooling rack, the helium line was removed and atmospheric air was allowed to diffuse into the retort. At the end of another hour, low-pressure dry air was allowed to flow through the retort for about 30 s, after which air pressure of about 5 lbf/in^2(ga) was maintained for 1 h. This exposure to air was designed to condition the titanium and slowly oxidize any of the fine filaments of magnesium that were usually present in the condensing area and which otherwise might cause fires during unloading.

The retort was moved to an unloading rack, and the entire string of retort head, retort furniture, and chip basket were lifted from the retort. The chip basket was weighed and placed in a conditioning storage can for another 6 h, so that any pyrophoric materials would have a chance to oxidize slowly, thus reducing their tendency to ignite while being removed from the retort basket. The retort and retort furniture were cleaned for reuse.

The bottom portion of the retorts gradually deteriorated from the alternate heating and cooling. The heated portions slowly oxidized, and during the later stages, heavy iron oxide scale began to fall away from the retort bottom. When the bottoms became thin or showed signs of caving in, the retort was rebuilt. Retort bottoms had an average life of 63 runs.

Crushing and Screening

Specifications for the sponge metal shipped required it to be of such size that at least 95 pct would pass a 0.5-in screen and not more than 1.5 pct would pass a 20-mesh sieve. Consequently, all of the sponge had to be crushed and sized after distillation. The chips always sintered together during distillation, and comminution of the refined sponge was a problem that was not completely solved. In most cases, the sponge was sintered loosely and fragmentatiion was accomplished easily. Occasionally, however, portions of a batch would be sintered together very firmly. In rare cases, slabs and pieces up to about 2 in thick would be compacted almost to solid metal and were very difficult to crush. Such pieces were broken into small fragments on a hydraulic press fitted with cutting chisels.

After cooling and conditioning of the charge, the chip basket was transferred to a steel chipping bin where the stainless steel basket wrap was removed. The sponge was removed from the basket skeleton frame using a pneumatic chipping hammer. The operation is shown in figure 45. The sponge was fed to the jaw crusher as it was chipped from the basket to minimize losses from fires that occasionally were started by the chipping operation.

From the jaw crusher, the sponge was transferred manually to an 18- by 36-in double-deck, suspension vibrating screen. The top screen had 0.5-in openings, and the lower screen was a Tyler standard 20-mesh screen. Oversize was returned to the jaw crusher manually, and the intermediate material fell onto a short 10-in conveyor, passed over a Ding's magnetic pulley, which removed any tramp iron present, and then dropped through a Tyler 16:1 sampler. This sample was run through the sampler a second time, yielding about a 1-lb sample that was used for chemical analyses and for preparation of an arc-melted button on which Brinell hardness was determined. The balance of the batch was transferred to a 40-gal shipping drum equipped with an airtight lid.

EXPERIMENTAL OPERATION

Substitution of Argon as an Inert Atmosphere (*14*)

One of the requirements for the production of ductile titanium was shielding of the metal from the atmosphere

Figure 45.—Breaking finished titanium sponge away from basket frame with an air tool.

whenever it was at elevated temperatures. Helium gas was used in all of the development work. Argon gas was a logical alternative to helium, as its potential availability is virtually unlimited because it can be extracted from air. The practical production of helium, on the other hand, is limited to extraction from natural gas. Argon is 10 times as dense as helium, and its thermal conductivity is about one-ninth and specific heat about one-tenth that of helium.

Approximately one-half of all the helium consumed in the demonstration plant was used in the reduction step; therefore, a series of experiments was conducted to determine the operational characteristics of this unit operation when argon was substituted for helium.

The major operational differences when using argon instead of helium were caused by clogging of vent and feed pipes and condensation of mixed chlorides on the pot lid and the surface of the reaction mass. This clogging and condensation was particularly troublesome in the early argon runs when operating procedures were the same as those used with helium. In these reductions, the temperature at the top of the reactor was 100° to 150° C lower than when using helium, undoubtedly because of the lower heat conductivity of the argon. By changing the air cooling at the top of the reactor, it was possible to maintain lid temperatures comparable to those encountered with helium. This alleviated clogging problems slightly, but they were still greater than when helium was used. Comparative operating data for argon tests and interspersed helium tests are given in table 24.

Table 24.—Operating data of argon test runs summarized progressively and compared with contemporary helium runs, averages per run

Group of runs	Feed time, h	$TiCl_4$ fed, lb	$MgCl_2$ tapped, lb	Lid temp, °C	Pokes per run	Runs requiring poking, pct
Argon:						
All runs	6.58	1,032	926	565	2.12	72.2
1st 20 runs	6.61	1,012	917	489	3.60	75
2d 20 runs	6.57	1,032	929	525	2.40	65
3d 20 runs	6.72	1,033	926	612	1.90	70
4th 20 runs	6.53	1,040	929	602	1.65	75
Last 28 runs	6.52	1,041	929	599	1.36	75
Helium: 32 runs	6.77	1,031	903	605	.56	25

The deposits that caused plugging when argon was used were distinctly different from those formed when helium was used. Deposits formed in helium runs were relatively dense titanium sponge containing some magnesium and $MgCl_2$. Vigorous effort with a steel bar was required to dislodge the deposits and reopen the line. When argon was used, the feed and vent lines repeatedly plugged with very soft, easily dislodged deposits; once plugging started, the necessary poking and cleaning accelerated subsequent plugging.

Other noticeable differences were the color and density of the exhaust-vent gases. With helium, the exhaust gases were generally light gray, somewhat resembling cigarette smoke. During the early stages of the argon tests, vent gases varied from black to brown, gray, green, purple, and even reddish at different times. Vent-line plugging was most frequent when these colored exhaust gases were thick. The highly colored gases clearly indicated the presence of lower chlorides of titanium. Chemical analyses of a number of plugs, although highly inconsistent, confirmed that the plugs from argon runs contained an appreciably higher percentage of chloride, whereas those from the helium runs had a higher proportion of metallic titanium and magnesium.

The metallurgical results from runs using argon and helium were not significantly different. The variance in magnesium efficiency, titanium recovery, and product quality was no greater than between random groups of helium runs. Although operational characteristics were appreciably different when argon was used, many operating statistics, such as feed time, feed rate, and average amount of feed per run, were virtually the same. The efficiency of $MgCl_2$ removal by tapping from the reduction pot was higher for the argon runs.

Methods for Improving Sponge Quality (*132*)

At the conclusion of demonstration plant operation for production of metal, a series of intermittent experimental operations was conducted to more firmly determine factors affecting sponge quality and to produce a higher quality sponge. No attempt was made to operate the plant continuously except in isolated instances where test procedures required more than regularly scheduled 10-day periods. The equipment was never operated at capacity, and experimental variations were limited to the equipment used in the continuous production operation. Primary efforts were directed toward using very pure feed materials and minimizing atmospheric contamination.

Control of Impurities in Raw Materials

Practically all of the impurities in the feed materials, $TiCl_4$ and magnesium, were concentrated in the titanium sponge; thus, the use of higher purity feed materials was a promising avenue for improving sponge quality.

Table 25.—Chemical analysis of magnesium, average weight percent of impurities

Grade	Fe	Mn	Si	C	N
Cell Mg	0.036	0.05	<0.005	0.02	0.001
Low Mn and Al . . .	.032	.003	<.003	.007	<.001
Low Fe and Mn . .	.02	.005	<.01	.007	.001

It did not seem feasible to attempt purification of the magnesium beyond the standard pickling treatment to remove the oxide film. To gain some knowledge of the effect of magnesium composition on sponge purity, three grades of commercial magnesium were used in reduction runs. Analyses of the three grades are given in table 25.

The average Brinell hardness and chemical analysis of the titanium sponge produced when using the three grades of magnesium are given in table 26. The different grades of magnesium had no significant effect on the hardness of the titanium sponge produced, nor were there significant variances in the metallic impurities except for manganese. Regular cell-grade magnesium yielded metal in the same hardness range as that made from magnesium with low iron, low manganese, and low aluminum.

The standardized technique for purifying $TiCl_4$ as described in chapter 2 was altered as follows: (1) sulfiding temperature was raised from 90° to 115° C, (2) the $TiCl_4$ was degassed by scrubbing with helium or argon, and (3) glass wool filters were placed in the feed lines leading to the reduction pot.

The effect of higher sulfiding temperatures was determined by comparing sponge from 12 runs using tetrachloride sulfided at 115° C, with sponge from the 16 runs using 90° C sulfided $TiCl_4$, which immediately preceded the 115° C runs, and the 16 runs using 90° C sulfided tetrachloride immediately following the 115° C runs. The product from the reductions using $TiCl_4$ sulfided at 115° C averaged 6 HB points lower in hardness than the product from the 90° C sulfided tetrachloride.

In succeeding tests, $TiCl_4$ sulfided at 115° C was scrubbed with helium both before and after sulfiding. The results of the sulfiding and degassing tests are shown in table 27 and indicate that degassing $TiCl_4$ reduced the hardness of the sponge significantly, even more so than the higher sulfiding temperature.

The glass wool filters trapped a dark-green residue. Qualitative analysis showed the major metallic impurity to be iron with lesser amounts of vanadium, aluminum, copper, nickel, calcium, and barium. No appreciable effect on product hardness could be attributed to use of the filters.

Control of Atmospheric Contamination

Table 27.—Effects of $TiCl_4$ purification techniques on hardness and sponge quality

[1]$TiCl_4$	Number of runs	HB	Impurity content, average wt pct: N	Cl	Mg	Fe	Mn	Si	V	[2]O
Untreated . . .	32	130	0.0070	0.058	0.093	0.059	0.060	0.049	0.03	0.175
Part treated .	12	124	.0065	.054	.089	.061	.048	.040	.03	NA
Treated	35	112	.0039	.048	.095	.078	.048	.030	.03	.130

NA Not analyzed.

[1] Untreated $TiCl_4$ sulfided at 90°C; part treated at 115°C; treated at 115°C and scrubbed.

[2] Number of runs does not apply to oxygen results.

Exposure to the atmosphere was a serious source of contamination in the magnesium reduction process. Although atmospheric gases contributed to contamination, exposure to moisture was the most serious source of contamination. Prevention of atmospheric contamination was pursued by experiments aimed toward (1) removal of air and moisture from processing vessel surfaces before application of heat, (2) purging of atmospheric gases from vessels prior to heating, (3) minimizing exposure to moist air, and (4) prevention of leaks and backflow of air during processing.

To minimize atmospheric contamination in the reduction operation, evacuation was started immediately after the pot was charged to the reduction furnace, and the pot was maintained for 1 h at 300° C under a vacuum of 27 to 28 in Hg. When this treatment was completed, the pot was raised to the reduction temperature while a constant helium purge was maintained. To diminish back diffusion of air into the pot during the reduction operation, oil seal bubblers were installed in the vent lines used to release pressure buildup in the pot. The tapping of $MgCl_2$ was terminated while there was still a molten layer of $MgCl_2$ above the taphole level instead of waiting for a helium blow as in the standard operation.

In the distillation operation, a decrease in contamination from contact with atmosphere was accomplished by a preheating-purging operation and an improved leak-check procedure. Before the basket of crude chips was loaded into a retort, the empty retort was heated under vacuum for 1 h at a temperature of 205° C. The retort was then loaded and purged with helium (or argon), charged to a holding furnace where it was heated for 2 h under vacuum at 205° C, backfilled with inert gas, and transferred to a furnace for the vacuum distillation cycle.

To ascertain the effects of the predistillation treatment and the prereducation treatments, a series of runs was made under three conditions. Degassed $TiCl_4$ was used in all runs. The results are summarized in table 28. The predistillation and prereduction treatments resulted in a definite improvement in sponge quality and gave a cumulative decrease in hardness of 10 pct.

Table 28.—Effect of pretreatment procedures on hardness of titanium sponge

Test condition	Number of runs	Average HB
Standard procedure	34	111.9
Pretreatment of distillation retort	41	103.0
Pretreatment of distillation retort and reduction retort	26	100.0

Table 26.—Types of magnesium versus titanium sponge quality

Type of Magnesium	Number of runs	Average HB	Chemical analyses, average wt pct: N	Cl	Mg	Fe	Mn	Si	V	Remarks
Cell Mg	130	104.2	0.0035	0.098	0.066	0.059	0.037	<0.005	<0.02	18.9 pct runs below 100 HB.
Low Fe and Mn . . .	134	105.1	.0046	.097	.061	.049	.010	.0086	<.02	24.6 pct runs below 100 HB.
Low Mn and Al . . .	90	111.8	0032	.089	.065	.060	.010	<.005	<.02	Operational techniques same as above, but $TiCl_4$ had some contamination by water.

Effect of Moisture on Hardness (*132*)

The major impurity contributing to the hardening of the titanium was oxygen, and the major source of oxygen contamination was water, either as a liquid or as moisture from the atmosphere. An excellent example of the effect of water contamination occurred when a water-cooled vapor condenser on the fractionating column of the $TiCl_4$ purification system developed leaks. Increased hardness of the titanium product was readily evident, but the cause was not discovered until the condenser finally failed. Study of the hardness trend showed that water had been leaking into the system for approximately 2 months before failure.

The moisture content of the dry-room atmosphere affected the quality of the titanium sponge despite the pretreatment techniques devised to minimize contamination. Correlation studies showed a definite relationship between humidity conditions and the Brinell hardness of the product. During the experimental operation, 139 of the 341 batches that had a hardness of 110 HB or less were handled in the dry room when the dewpoint range was -40° to -65.5° F. Indications were that the dewpoint of the dry room should be maintained at a maximum level of -40° F to produce metal with a consistently low hardness level.

Effect of Lower Chlorides on Hardness (*132*)

Lower chlorides of titanium, mostly present as $TiCl_2$, had a deleterious effect on the hardness of titanium sponge. The mixture of $TiCl_2$ and $TiCl_3$ was usually formed at the end of a reduction run when there was a deficiency of magnesium. Correlation studies showed that in batches of titanium with a hardness of less than 102 HB, lower chlorides were always absent. However, lower chlorides were present in 69.2 pct of the batches with a hardness greater than 120 HB. The reaction between lower chlorides and moisture appeared to proceed at a rapid rate, as evidenced by evolution of heat and smoke. The odor of HCl gas was usually present, and an oxychloride product was probably formed, which would be an additional source of oxygen contamination.

Formation of lower chlorides could be minimized by careful control of $TiCl_4$ feed rates, thus avoiding force feeding, especially near the end of a reduction operation.

SUMMARY OF DEMONSTRATION-PLANT OPERATION

The operation of the demonstration plant was divided into three distinct periods. From June 1952 to May 1953, the operation consisted largely of shaking down the equipment, training personnel, and developing acceptable operating procedures for continuous production under the sponsorship of the Ordnance Corps, Department of the Army. From June 1953 to September 1954, the plant was put on a production schedule of 360,000 to 500,000 lb of usable ductile titanium sponge to fulfill a contract with the Defense Materials Procurement Agency. In May 1955, the Wah Chang Corporation of New York and the Bureau entered into a cooperative agreement to develop methods for producing improved titanium sponge. The plant was operated intermittently under this agreement from June 1955 until September 1956. A summary of plant production is given in table 29.

Table 29.—Summary of production in demonstration plant

Sponsor[1]	Time period	Number of reductions	Sponge product, lb	
			Acceptable	Offgrade
Army Ordnance	6/52-5/53	327	77,180	3,279
DMPA	6/53-9/54	1,971	492,503	4,208
Wah Chang	6/55-9/56	960	220,611	([2])

[1] Under contract or cooperative agreement.

[2] Not recorded.

Table 30.—Summary of hardness and chemical analysis

Sponsor[1]	HB, pct of batches			Analysis, pct		
	140 or under	141-180	181 or over	Fe	Cl	N
Army Ordnance	24.9	69.9	5.3	0.081	0.111	0.014
DMPA	29.2	63.5	7.3	.097	.118	.012
Wah Chang	96.8	2.8	.4	.072	.095	.004

[1] Under contract or cooperative agreement.

Table 31.—Hardness and analysis of titanium sponge produced under Wah Chang agreement, percent

HB range	Total of runs, pct	N	Cl	Mg	Fe	Mn	Si	V
100 and under	8	0.0032	0.092	0.059	0.049	0.019	0.0071	<0.005
101 to 111	36	.0039	.094	.063	.057	.024	.009	<.005
111 to 121	31	0041	.095	.065	.072	.030	.016	<.005
121 to 131	15	.0062	.100	.070	.080	.039	.023	<.005
131 to 141	7	.0081	.097	.070	.091	.061	.035	<.005
141 to 151	2	.0160	.101	.069	.100	.052	.029	<.005
151 and over	1	.022	.095	.068	.130	.064	.037	<.005

The quality of the metal produced during the three operating periods is summarized in table 30, and a further classification of the metal produced under the Wah Chang cooperative agreement is given in table 31.

Demonstration plant titanium sponge production operations fulfilled most of the major objectives of this research campaign. Large quantities of ductile titanium were produced on a regular basis. Production of high-quality metal depended primarily on use of highly purified reactants, avoidance of contamination from the atmosphere and moisture during all phases of reduction and distillation, and reduction with sufficient excess magnesium to prevent formation of lower titanium chlorides. Continued improvements in these aspects of operations resulted in increased quality of the metal produced as the campaign progressed, as summarized in table 30.

CHAPTER 5.—MODIFIED MAGNESIUM REDUCTION TECHNIQUES

The magnesium reduction of $TiCl_4$ had proved a satisfactory method for producing ductile titanium metal. The process as developed in the pilot plant was a batch process that required much material handling with the resulting opportunities for contamination. The batch process also resulted in a product with considerable variation in quality from batch to batch. There was a potential for reducing production costs if a satisfactory continuous reduction method could be devised.

At the conclusion of the pilot-plant operations and coincident with the construction and operation of the demonstration plant, a number of alternative reduction methods were investigated with the objectives of reducing production costs and producing metal of higher and more consistent quality. Attempts to improve the magnesium reduction process were divided into two major lines of attack: (1) modification of the batch process to increase the output per batch and (2) development of a continuous reduction method.

MODIFIED BATCH REACTORS

At the Bureau's Albany (OR) Research Center, the production rate of zirconium by magnesium reduction of its chloride had been increased by adding a second charge of magnesium after the $MgCl_2$ was drained off and before the reactor was cooled. Application of this technique to titanium was questionable because of the ease of formation of lower chlorides of titanium. However, the prospect of increasing production per batch without change in size or type of equipment was considered sufficient justification for testing the technique. The top of a reduction retort used in previous pilot-plant reductions was modified by addition of an extra column for addition of magnesium. Reductions were conducted according to the normal demonstration plant procedure, followed by a second stage in which additional magnesium and $TiCl_4$ equal to approximately one-half of the initial charge were added. Two of these double-reduction runs were made, and both were successful to the extent that magnesium efficiencies of 78 and 82 pct were attained. Slower feed rates were required during the second stage of the reductions to prevent excessive pressure buildup. The inside of the columns, the lid, sides of the pot, and the surface of the reaction mass were coated with lower chlorides from the reduction in which the higher magnesium efficiency was attained. No attempt was made to recover and refine the sponge from these reductions, but the physical appearance of the reaction masses and the excessive formation of lower chlorides indicated that the product quality would be lower than for single-stage reductions.

An obvious method of increasing batch size was the use of a larger reactor. An increase in the reactor size also gave promise of a higher quality product. The capacity of the lathe used for removing the reaction mass limited the size of the retort that could be tested to 40 in ID by 36 in deep. This reactor would yield approximately 500 lb of titanium per batch using the standardized reduction technique developed for the 200-lb reactors.

Two reductions were made in a 500-lb-capacity reactor. The reaction mass at the conclusion of the reductions differed from that usually obtained in the 200-lb-capacity reactor in that relatively little of the mass stuck to the sides where it originally bridged. Most of it had dropped to form a flat layer about 9 in thick, the upper surface of which had four protuberances that were positioned directly below the four $TiCl_4$ feed pipes. The metal below each of the feed pipes was much more dense than the rest of the sponge. The average quality of the sponge produced in the 500-lb reactor was no better than that produced in similar 200-lb reductions. In the opinion of the operators, the larger reactor was easier to operate.

DESIGN AND OPERATION OF CONTINUOUS REACTORS

Conveyor Removal of Product

A 200-lb-per-batch reduction retort was modified in two ways to remove the titanium metal during operation. First, a cutter was provided to remove the sponge deposited on the walls so that it would fall to the bottom. Second, a receiver was connected to the bottom of the reaction chamber by an upward inclined chute through which the sponge could be raked up from the bottom of the reactor and into the receiver.

On short runs, the equipment gave encouraging results. However, it was clearly evident that unless the rake could be operated mechanically, the labor requirement would be so high that the method would have no advantage over the conventional batch-type operation.

A reactor was constructed as shown in figure 46. The lid was equipped with a cutter mechanism and a gate valve for adding magnesium. A spiral conveyor with an upward slope of approximately 13° extended from the bottom of the reduction retort to a discharge chamber surrounded at the bottom with a water jacket. A slag pot was attached at the lower end of the conveyor to drain $MgCl_2$ from the system when it attained the level of the pipe leading to the slag pot. A run was started and 170 lb of magnesium and 284 lb of $TiCl_4$ had been added when the shaft to the conveyor twisted in two. Disassembly of the reactor and conveyor showed that reaction products had deposited on and adhered to the conveyor casing and on the spirals of the conveyor so that it was almost plugged at the lower end. A pillar of metal 9 in high had also built up on the bottom of the reactor immediately below the $TiCl_4$ feed pipe. A portion of the product from this reactor was refined by vacuum distillation, and a light, fine-grained, porous sponge was obtained that had a hardness of 475 HB when melted into a test button. The adherent nature of the reaction products indicated that continuous removal of product from a conventional reactor was not a promising method for reducing process costs or improving quality.

Liquid Curtain Wall Reactor

The most sophisticated attempt to design a continuous reactor provided for reaction chamber surfaces protected by a curtain or film of molten $MgCl_2$ to prevent accretions on the walls. A diagram of the apparatus is shown in figure 47. The operation was supposed to proceed as follows: After loading the magnesium chamber with ingots and the lower reservoir with enough $MgCl_2$ to

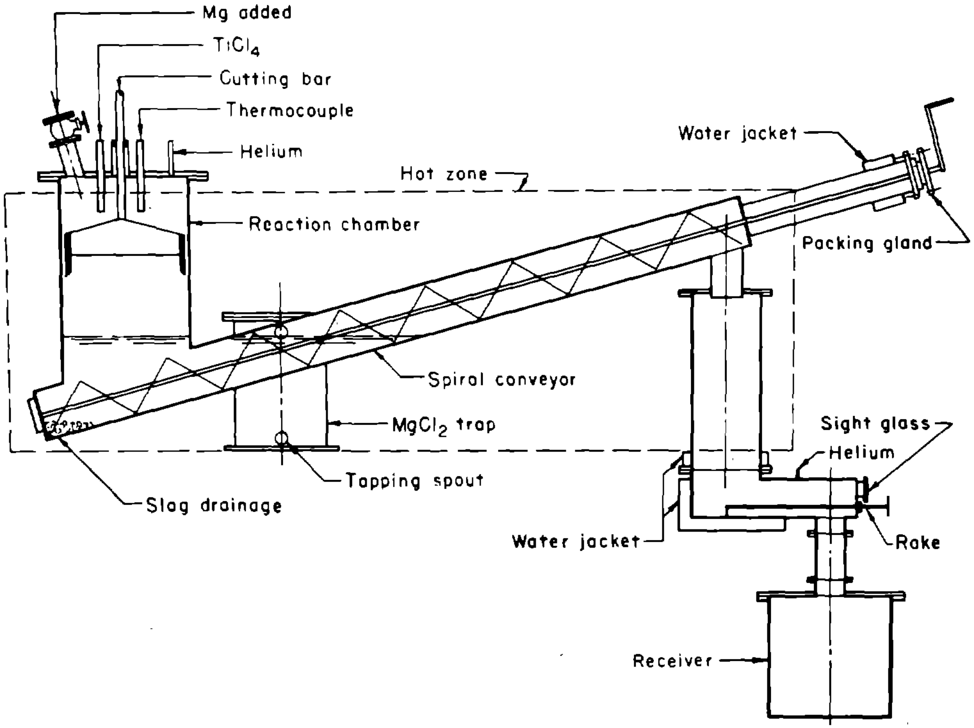

Figure 46.—Batch reactor with spiral conveyor for removal of product.

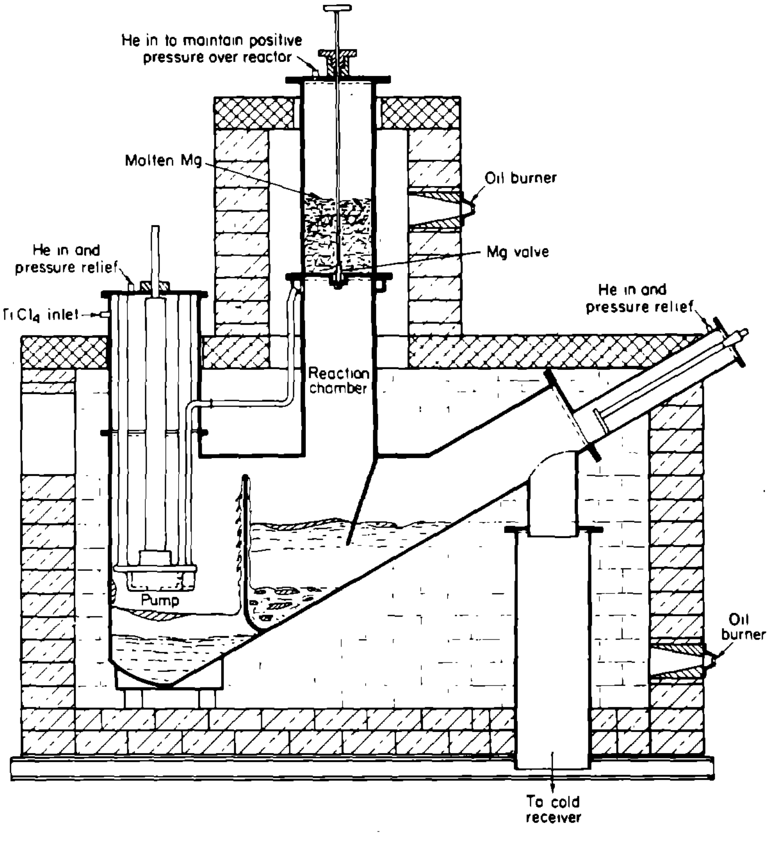

Figure 47.—Section of furnace detail.

establish a bath level after fusion, the apparatus was sealed, air inside was replaced with helium, and the temperature was raised to 750° C. The pump was started to discharge molten $MgCl_2$ down the walls of the reaction chamber, and finally a stream of magnesium was admitted to the reaction chamber while $TiCl_4$ was admitted through the top of the pump chamber.

It was hoped that a granular product would be formed that would be guided by the perforated baffles into the pocket below the reaction chamber from which it could be raked into a receiver for removal. In operation, the product proved to be the usual adhesive mixture of finely divided titanium and magnesium. It clogged the perforated baffles so that the $MgCl_2$ had to flow over the top of the baffles to reach the pump. Deposits were also found in the pump and in the $MgCl_2$ distribution channel at the top of the reaction chamber.

Magnesium Droplet Reactor

Numerous attempts were made to produce titanium metal by introducing droplets of magnesium metal into a reactor filled with titanium chloride vapor. The objective was to form a granular titanium metal that would be amenable to continuous removal. The exploratory tests were made in reactors constructed of sections of iron pipe. The top section was the molten magnesium feed pot. The central section was the heated reactor into which $TiCl_4$ and magnesium metal were introduced simultaneously, and the bottom section was a cooled receiver for collecting the product. The problems encountered in the exploratory tests were (1) plugging of the magnesium orifice by solid impurities in the magnesium, (2) formation of accretions around the magnesium valve, (3) formation of accretions on the walls of the reaction chamber, (4) low utilization of magnesium, and (5) excessive formation of lower chlorides.

Increasing the size of the magnesium orifice remedied the plugging problem but produced larger magnesium globules, which resulted in decreased magnesium efficiency. The use of a filter made up of titanium turnings and placed immediately above the orifice satisfactorily removed impurities from the magnesium so that a 0.040-in-diam opening could be used. The construction of an annular helium jet around the bottom of the magnesium valve orifice prevented the buildup of accretions.

The problem of formation of accretions on wall surfaces was persistent. Inspection and analysis of the accretions indicated the formation of a very sticky, viscous material at some stage in the reaction. Analysis indicated that the material was largely a mixture of titanium and magnesium, well drained of $MgCl_2$. The various reactor modifications tested to overcome or utilize this property were as follows: Increases in the diameter, length, and shape of the reaction zone; installation of a shaker pan to increase reaction surface; installation of a removable product collection target; and changes in the location in which gases were introduced and removed.

Increasing the diameter of the reaction zone alleviated the buildup of accretions on the walls in that, as the diameter increased, the buildup started at a lower level. The construction of a reactor with a long reaction zone of increasing diameter toward the bottom (frustrum of a cone) resulted in a reduction in which no wall accretions were formed. The reaction mass in the receiver section was the usual stratified mass of titanium, magnesium, $MgCl_2$, and lower chlorides of titanium. In one experiment, a shallow, vibrating iron pan was installed directly under the magnesium orifice to take advantage of the tendency of the reduction to occur on a surface. The object was to shake the product off by a directional shaking movement of the pan so that it would fall into the receiver below. When the reactor was opened, most of the product was found adhering to the pan and on the reactor wall area corresponding to the throw area of the pan motion. In another experiment, a circular iron disk was installed at the bottom of the reaction zone to act as a product collector. The purpose was to form a metallic stalagmite that could be withdrawn from the furnace at appropriate intervals. Metal did build up on the target but lacked the stiffness required to form a stalagmite, and much of the product flowed over the sides of the disk. The product consisted of a dispersed mixture of finely divided titanium and magnesium, the same type of material that adhered to the walls of reaction zones.

Rotary Reactor

A horizontal rotary reactor was tested that contained titanium blocks intended to act as metal accumulators. The chamber was loaded with an appropriate amount of magnesium, together with a charge of 2-in cubes of titanium that had been pretreated at 1,000° C in magnesium to reduce the oxide film on the surface and to coat them with magnesium. It was hoped that the sticky nature of the freshly formed titanium would cause it to adhere to the blocks, which could be removed and replaced with new small blocks when they had reached a predetermined size. The furnace was heated to 750° C, and $TiCl_4$ was introduced through one of the shafts while the reactor rotated. Figure 48 shows the chamber after opening. The product had adhered as much or more to the walls of the reactor as it had to the titanium blocks.

A second test was performed in the same reactor. The chamber was charged with cubes of magnesium that were heated to a temperature slightly below their melting point. It was hoped that a lightly adhering powder would form that would flake off the tumbling blocks as the drum revolved and could be removed through one of the trunions. Titanium tetrachloride was added at the desired rate for a short time until the rate of reaction decreased rapidly. Inspection of the reactor contents showed that the magnesium cubes were covered with a rather impervious, adherent film of titanium lower chlorides. There was no indication of formation of titanium metal.

During attempts to develop a continuous reaction process, many of the operational difficulties encountered were gradually overcome through changes in equipment design and operating technique. The problems of low magnesium utilization and a high proportion of lower chlorides of titanium in the product resisted all remedial measures and appeared to be fundamental characteristics of the techniques investigated. Attempts to develop a continuous reduction process with magnesium metal as a reductant were therefore terminated.

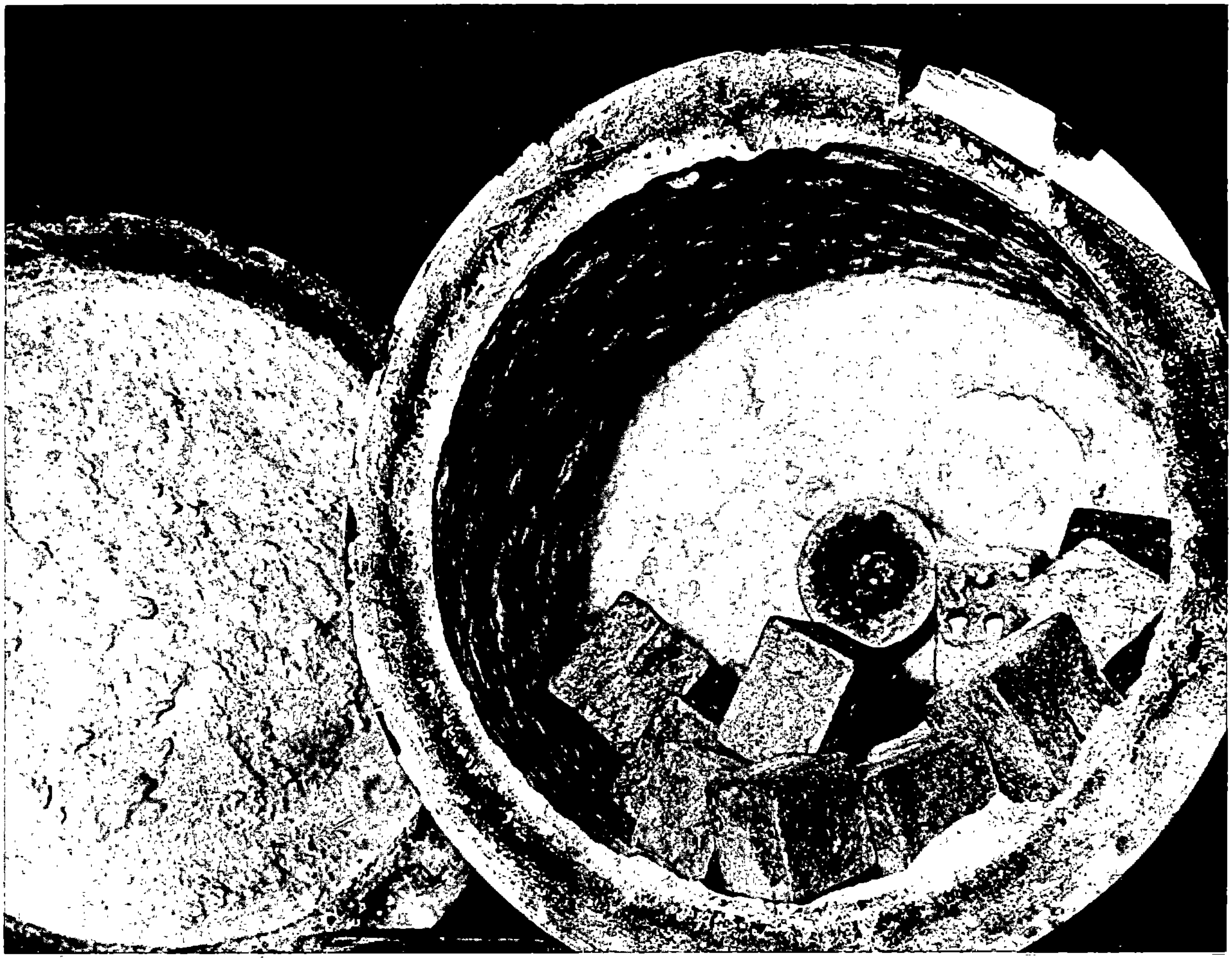

Figure 48.—Sixteen-inch-diameter revolving chamber opened to show metal adhering to wall.

CHAPTER 6.—SODIUM REDUCTION OF TITANIUM CHLORIDES

The physical properties and availability of metallic sodium indicated that it would offer several advantages for producing metallic titanium by reduction of $TiCl_4$. The sodium reaction is more exothermic than the magnesium reaction and has a more negative free energy. The higher volatility of sodium metal offered a possibility of improvement in removal from the pores of the titanium metal product. The low melting point of sodium would facilitate purification, handling, and feeding of the reductant. Both the metal and the NaCl reaction product are readily soluble in water, thus allowing a simple leaching operation for recovery of the titanium metal product.

The use of sodium also has certain disadvantages. Because sodium is monovalent and has almost as great an atomic weight as magnesium, nearly twice as much sodium is required per pound of titanium reduced. Also, the flammability of sodium and the caustic nature of its oxide require extra safety precautions in its use.

The sodium used in the reduction research was a commercial product supplied in drums sealed under argon. Specifications were: Metallic sodium, 99.0 pct min; calcium, 0.04 pct max; chlorides (calculated as NaCl), 0.01 pct max; and sulfates and heavy metals, none. Suppliers stated that in most cases, the metal quality exceeded specifications; and analyzed greater than 99.95 pct Na, with calcium as the major impurity. The sodium was removed from the drums by melting and transferring by argon gas pressure, usually through a 10-µm-pore-size stainless steel filter element. A residual layer was left in the bottom of the drum to prevent transfer of settled impurities.

The direct one-stage reduction takes place according to the reaction

$$4Na + TiCl_4 \rightarrow 4NaCl + Ti, \qquad (23)$$

and the two-stage reduction according to

$$2Na + TiCl_4 \rightarrow 2NaCl + TiCl_2 \qquad (24)$$

and

$$2Na + TiCl_2 \rightarrow 2NaCl + Ti. \qquad (25)$$

Depending on the conditions, many side reactions are possible. Among these are

$$Na + TiCl_4 \rightarrow NaCl + TiCl_3, \qquad (26)$$

$$2TiCl_3 + Ti \rightarrow 3TiCl_2, \qquad (27)$$

$$TiCl_4 + Ti \rightarrow 2TiCl_2, \qquad (28)$$

$$2TiCl_3 \rightarrow TiCl_2 + TiCl_4, \qquad (29)$$

and

$$2TiCl_2 \rightarrow TiCl_4 + Ti. \qquad (30)$$

During the course of the Bureau research at Boulder City, NV, using sodium as the reducing agent, all of these reactions were observed except 30, the disproportionation of $TiCl_2$. In practice, it was difficult to maintain stoichiometric introduction of the reactants into the reaction zone as indicated by the equations. All of the reactions except the disproportionation reactions are exothermic, and the reaction zone temperatures varied considerably with change in feed rates and proportions of the reactants, causing variations of both the predominating reaction during a feeding period and the product mix. During runs in which the proportions of sodium and $TiCl_4$ shown in reaction 23 were approximately maintained, the product was, without exception, either fine powder or a sponge mass, depending on the reactor configuration.

Reaction 24 represents the first stage of the deliberate two-stage reduction of $TiCl_4$ by sodium. In experiments in which the reactants were introduced in the proportion indicated by this reaction, reactions 23 and 26 always occurred to some degree with the production of variable amounts of titanium powder and $TiCl_3$ along with the predominating, dark green NaCl-$TiCl_2$ salt mixture. Holding the reaction products for a period of time at a temperature above their melting point promoted reaction 27, and by using this procedure, it was possible to obtain melts in which the average effective valence (AEV) of the soluble titanium was between 2.1 and 2.3.

Reaction 25 constitutes the second step of the two-stage reduction procedure. Reaction 28 was used to raise the $TiCl_2$ content of the melt obtained in reaction 24. Use of titanium scrap as the metal reactant provided a procedure for recycling scrap. In the course of the experimental work, reaction 29 was occasionally observed.

LOW-TEMPERATURE REDUCTIONS

Ball-Mill Reactors (*97*)

Preliminary tests at temperatures slightly above the melting point of sodium resulted in low sodium utilization caused by coating of the sodium with a nonreactive crust of salt, fine titanium, and lower chlorides of titanium that prevented further reaction. To overcome this difficulty, three ball-mill-type reactors were constructed. These mills were externally heated rotating chambers in which titanium blocks or iron balls were used to break up the crusts that formed on the sodium surfaces.

The first ball-mill reactor consisted of a horizontal, 10-in-diam, mild steel, cylindrical center section assembled to mild steel belled ends by welded flanges. This mill was heated either by rotating it in a hot oil bath or with propane-gas burners. Sodium metal was fed intermittently from an electrically heated chamber and allowed to react with a weighed quantity of $TiCl_4$ fed as a liquid through a flowmeter while the reactor was rotating. It was necessary to stand the mill on end to remove the product. Accretions of reaction products and unreacted sodium adhered to the wall of the reactor.

A larger diameter, conical-end, batch reactor was fabricated to overcome these disadvantages, and although this mill was easier to unload than the first model, it was difficult to remove the product without affecting its purity.

Several rotating reactors designed for continuous operation were constructed and tested but were unsuccessful because of failure of packing glands or rotating seals. Work on ball-mill reactors was suspended because of contamination of the product and because of mechanical difficulties that developed when expansion to a larger scale continuous process was attempted.

High-Surface Sodium Reactors (56)

In 1953, the U.S. Industrial Chemical Company published information (*209*) on a low-temperature sodium reduction technique that involved the use of a sodium coating on finely divided inert solids. A similar technique was reported by Quin in 1954 (*169*). The term high-surface sodium (HSS) was applied to films of sodium approaching colloidal dimensions (0.5 to 1,000 nm) spread over inert solids of high surface area.

Initial experiments using the HSS principle were conducted in horizontal batch reactors. The free-flowing properties of the products indicated the possibility of continuous removal. A vertical reactor was developed in which continuous automatic feeding of the reactants and discharging of the products were attained. A schematic drawing of the apparatus is shown in figure 49.

Purified $TiCl_4$ was stored under helium in a steel drum that was connected to a 2-gal steel feed container mounted on a scale. The outlet of the weighing container was connected to a flowmeter that discharged into a mild steel boiler. The vaporized tetrachloride was fed to the reactor. The boiler and the pipe carrying the vaporized tetrachloride were electrically heated.

Commercial sodium was melted and charged under argon to a heated mild steel pot. Liquid sodium was transferred to the reactor through a ½-in mild steel pipe connected to the bottom of the sodium pot.

The reactor was fabricated from a mild steel pipe section, 14 in. in diam and 9 in high. A baffled jacket was provided at the walls and the bottom of the reactor. A U-shaped, motor-driven, mild steel mixing paddle was installed in the reactor with ⅛ in of wall clearance. A pump circulated a heat-transfer medium through the reactor jacket and through a water-cooled heat exchanger when cooling of the reactor was desired. The heat exchanger was bypassed and gas burners under the reactor were used to supply heat when heating of the reactor was required.

For discharging the product, a 2-in-diam pipe was connected to the reactor wall 1 in from the top. This pipe housed a horizontal, motor-driven screw conveyor that

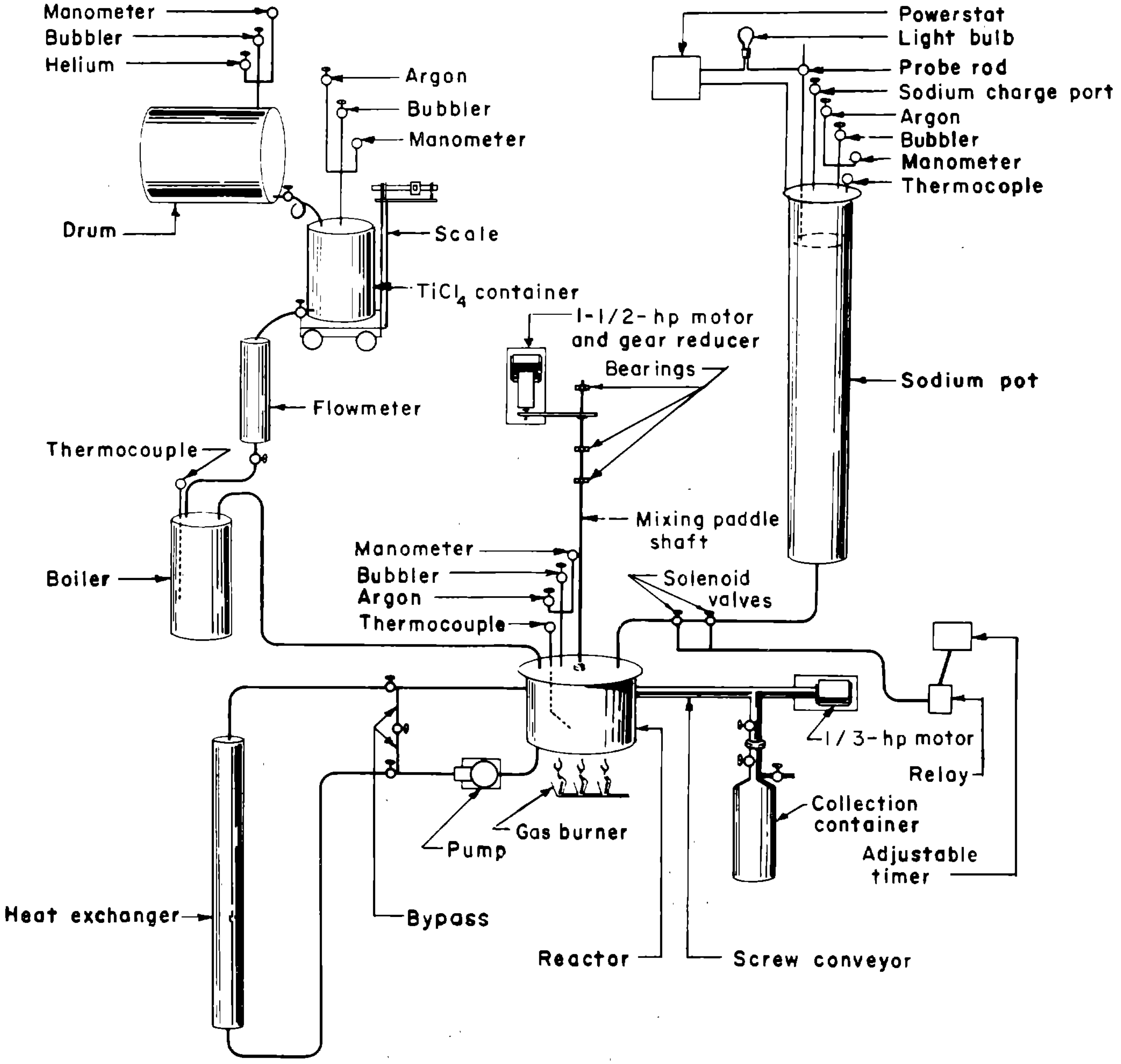

Figure 49.—Schematic drawing of apparatus.

discharged the product into a vertical tube connected to the product collection container through double ball-type valves. This permitted the product collection container to be attached or detached with minimum atmospheric contamination of the product and the reactor system.

Experimental Procedure

Approximately 9 lb of dried, minus 100-mesh, CP-grade NaCl was charged into the reactor. The reactor was heated to 110° C, evacuated to approximately 27 in Hg for 2 h, and then backfilled with argon. The mixing paddle was then set in rotation at 175 r/min to stir the bed of NaCl.

About 3.5 oz of sodium was added to coat the NaCl before starting the $TiCl_4$ feed. Argon pressure of 3 $lbf/in^2(ga)$ was maintained in the sodium pot and the $TiCl_4$ container. Shortly after the start of the tetrachloride feed, heat generated by the reaction caused the temperature and pressure in the reactor to rise. The pressure was relieved to 0.25 $lbf/in^2(ga)$ through an oil bubbler to maintain an approximately constant pressure difference between the feed systems and the reactor to avoid excessive fluctuations in the feed rates. When the temperature in the reactor reached 160° C, the gas burners were turned off, and the heat transfer medium was circulated through the water-cooled heat exchanger to maintain the reactor temperature between 105° and 205° C. Finally, the motor powering the product discharge conveyor was turned on to carry the product to the collection chamber. Thus, the HSS reactor was set in continuous operation. To remove the product, the valves on the product-discharge tube and the neck of the collector were closed, and the collector was detached. The product was unloaded in an airtight box under argon.

For subsequent operations, the powder retained in the reactor was used as the HSS carrier. When a different reaction product was desired, such as titanium lower chlorides or a mixture of titanium lower chlorides and metallic titanium, the sodium-to-titanium tetrachloride feed ratio was adjusted to the corresponding values. When the feed ratio was changed to produce a different product, about four times the weight of the material retained in the reactor had to be put through the reactor before the product reached a constant composition.

Experimental Results

Reductions using sodium-to-titanium tetrachloride mole ratios in the range of 1.9 to 3.9 were made in the HSS reactor at temperatures between 105° and 205° C. When using feed ratios in the range of 2.4 to 3.3, the sodium and $TiCl_4$ feed rates and the product-discharge rate remained fairly constant, once the regulating instruments were adjusted. In operations using feed ratios of 1.9 and 3.9, frequent adjustments of the regulating instruments were required because of the pressure fluctuations that occurred.

The reaction products as discharged from the reactor were in the form of fine particles in the micrometer-size range. They were very reactive in air but could be handled safely in an inert atmosphere. Analytical data on the products, representative of operations using various feed ratios, are shown in table 32. Samples were taken after steady-state conditions had been attained in the reactor. Attempts to extract pure titanium metal from the powdery product mixture containing salt and metal by leaching or vacuum distillation proved unsuccessful.

Operation of the HSS reactor provided a continuous method of producing an $NaCl$-$TiCl_2$ mixture for further reduction on a batch basis in the second stage of the two-stage process. This product could also be used as a source material for preparing electrolytes for the electrorefining of titanium metal (*145*), a process investigation that was conducted concurrently with the active metal reduction research.

SINGLE-STAGE REDUCTIONS

The first high-temperature sodium reductions were conducted in reactors in which the $TiCl_4$ was bubbled into molten NaCl, and the sodium was fed onto the surface of the melt. Numerous variations of the "liquid-filled" reactor were tested, but the product was always a finely divided material that yielded a sponge with high hardness and a high iron content. Typical hardness of a test ingot was 310 to 340 HB, and the iron content ranged from 3 to 6 pct.

The second type of reactor tested in the high-temperature reduction of $TiCl_4$ with sodium was similar to the droplet type reactor that had proved unsuccessful in magnesium reductions (see chapter 5) because of sticking of the product to reactor walls, low magnesium utilization, and excessive formation of lower chlorides of titanium. In the previous sodium reductions, it was observed that sodium was less inclined to wet metal than was magnesium; this, coupled with the higher heat of reaction with sodium, indicated that problems encountered in the magnesium reductions might be alleviated by substitution of sodium. Reductions were conducted in $TiCl_4$-vapor filled reactors with hot bottoms, with cold bottoms, and with perforated collection baskets for separation of the titanium and sodium chloride products.

The reaction mass recovered from the hot-bottom reactors consisted of a conical heap of partially sintered fine-grained metal in the center surrounded by NaCl that was relatively barren of titanium or titanium lower chlorides. Separation of the reaction products by use of a metal basket with a perforated bottom was unsuccessful because of the fineness of the metal product. An excessive amount of salt was trapped in the material remaining in the basket, and some of the fine metal was carried along with the salt that drained off. In addition, lower chlorides were formed that collected between the walls of the reactor and the basket, and the excess sodium remained in the basket and on the bottom of the reactor. In the cold-bottom reactors, the product composition was very erratic, with variable quantities of salt, titanium, and sodium metal.

Table 32.—Analyses of as-discharged products, percent

Feed, Na-$TiCl_4$ mole ratio	Na	Cl	Total Ti	Soluble Ti
4.0	36.2	44.8	15.1	0.03
	33.8	47.5	15.5	.12
3.9	35.7	45.5	15.3	0
3.4	30.6	49.7	16.5	3.56
	30.1	49.4	17.3	1.98
3.3	32.6	49.3	17.2	1.75
2.7	23.9	55.7	18.6	9.86
	21.6	57.4	19.6	13.4
	23.7	56.2	19.0	12.1
2.3	22.1	56.8	19.8	16.8
	23.1	55.9	17.8	15.1
	23.1	57.9	19.2	16.5
2.0	21.4	57.9	19.8	16.1
	19.1	59.9	20.1	16.4
	20.0	58.4	19.6	16.9

TWO-STAGE REDUCTIONS

In the operation of the metal droplet reactors, it was seldom possible to maintain the sodium metal and $TiCl_4$ feed rates in the proportions required by reaction 23. Whenever reactors were opened after a run in which the sodium to $TiCl_4$ ratio was below 4, $TiCl_2$ was a product component, and as the ratio decreased, the proportion of dichloride increased, as evidenced by the color of the salt. Subsequent additions of sodium to molten reaction products containing large proportions of dichloride yielded a titanium product that contained discrete needles and crystals of titanium metal. Hardness tests on segregated fractions of the crystalline product gave values of less than 110 HB. It was also observed that, as the proportion of dichloride in the intermediate reaction product increased, the proportion of the coarse fraction of crystals from the second reduction increased. For these reasons, research was directed toward development of a two-stage process.

A typical two-stage reduction entailed the following operations:

1. Reduction of $TiCl_4$ vapor with sodium with the reactants proportioned as shown by reaction 24, the furnace temperature at 700° C, and the internal reaction zone temperature held at <800° C as much as possible by controlling $TiCl_4$ feed rates.
2. Soaking of the first-stage reaction product for 15 to 24 h at 600° to 900° C to promote the formation of $TiCl_2$ by reaction 27.
3. Addition of sodium to the first-stage melt in the proportions shown by reaction 25.
4. Soaking of the second-stage product for 12 to 20 h at 825° C.
5. Addition of a small amount of $TiCl_4$ before tapping of salt to react any free sodium.
6. Separation of salt from the metal product by tapping.
7. Leaching of reaction products in dilute HCl solution.
8. Separation of products by size and form.

The first step in the research was the determination of variables that affected the properties of sodium chloride-titanium lower chloride melts.

Production of Titanium Lower Chlorides (96)

Equipment

Reactors

Figures 50 and 51 show sectional views of two general types of reactors employed in the production of titanium lower chlorides. The diameters of the reactors ranged from 6 to 30 in. All reactors consisted of a reaction chamber and a salt chamber that were separated by a diaphragm. The reactors were made of type 316 stainless steel. In reactors 19 in or larger in diameter, diaphragms were made of 14-ga stainless steel, and in smaller reactors of 20-ga mild steel. A thermocouple, protected by a stainless steel tube, was inserted into the reaction chamber through a packing gland to measure the melt temperature. In the simple diaphragm reactors, a pointed rod was installed that could be pushed down to puncture the diaphragm, thus allowing the melt to drain into the salt chamber below. A $TiCl_4$ feed pipe was installed through a packing gland to permit the feeding position inside the reaction chamber to be changed. This pipe was also connected to a helium source

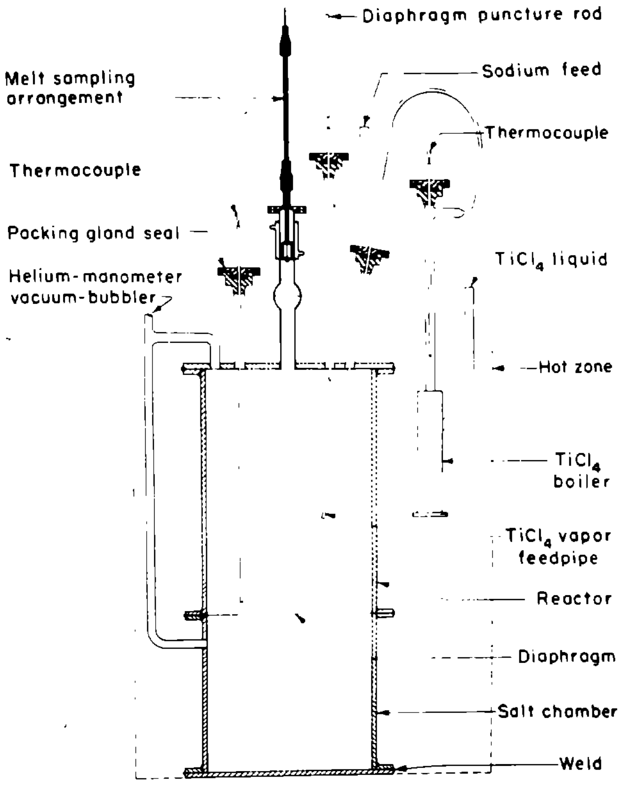

Figure 50.—Weir-type diaphragm reactor.

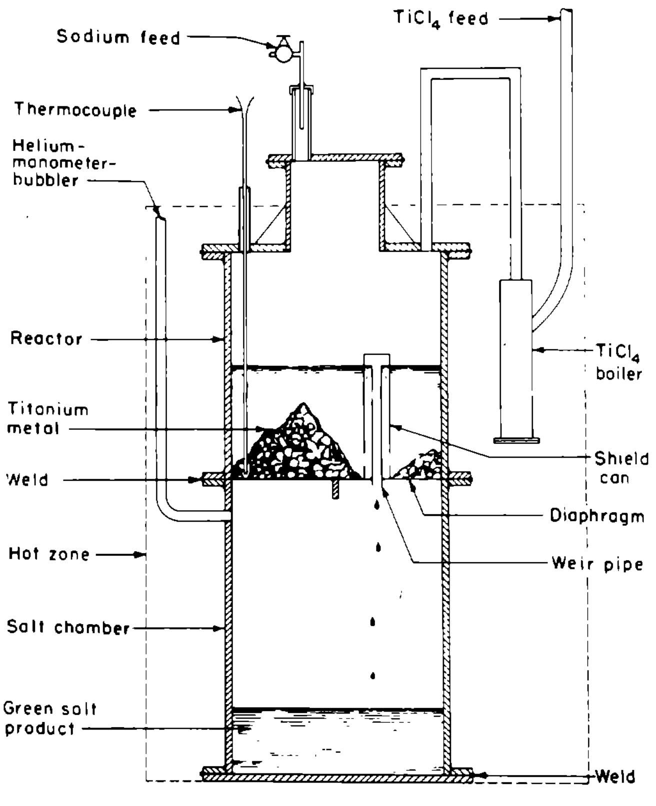

Figure 51.—Simple diaphragm reactor.

and could be used to bubble helium through the melt after feeding $TiCl_4$.

Depending on the cooling of the lids, reactors were designated as cool-top and hot-top reactors. The cool-top reactors were installed with the lid extending 7 in out of the hot zone of the furnace. In the hot-top reactors, the lid and the reaction chamber were welded together, and the lid of the reactor was installed within the hot zone of the furnace.

Furnaces

A furnace 24 in wide by 26 in long and 6 ft high was used for heating the 12- to 19-in-diam reactors. It was constructed of insulating bricks and had a removable front section to facilitate installation of the reactors.

In the tests with a 30-in-diam reactor, a gas-fired furnace 66 in. in diameter and 63 in high was used.

Furnace temperatures were measured by thermocouples installed in stainless steel protection tubes, which were butted against the side of the reactor at three vertical positions. The temperature given in this report were those taken at the middle position, about 6 in above the reactor diaphragm, corresponding to the reaction zone of the reactor.

Titanium Tetrachloride Boiler

The $TiCl_4$ boiler was fabricated from AISI Type 316 stainless steel pipe, 2 in. in diam and 20 in long, with 1-in-diam inlet and outlet lines. The boiler was installed in the furnace with the reactor; therefore boiler temperature was dependent on furnace temperature. A larger model of this boiler, 3 in. in diam and 24 in long, was used with the 30-in-diam reactor.

In all tests, liquid $TiCl_4$ was fed to the boiler through a flowmeter from a weighed storage tank.

Inert Gas Purifiers

Purifiers for helium and argon were constructed from 2-in-diam stainless steel pipe, and were 2 ft long. Turnings of a titanium-zirconium alloy were used as the getter. The purifiers were electrically heated to maintain a temperature of about 400° C.

Sodium Feed Chamber

The sodium feed chamber was made from mild steel, was 19 in. in diameter by 4 ft high, and was heated by Nichrome resistance units. The sodium inside was blanketed by purified argon gas. The feed chamber, connected to the reactor with a flexible steel hose, was installed on a scale, and the sodium entered the reactors through valves located above the reactor lids.

Experimental Procedures and Results

The degree of conversion of the $TiCl_4$ to $TiCl_2$ was inferred from the determination of the average effective valence (AEV) of the soluble titanium in the reaction products. The method for determining AEV is discussed in chapter 10.

Sodium Reductions

All interior surfaces of the reactor and pipes were thoroughly cleaned. The reactor was assembled, tested for leaks, and installed in the furnace. The reactor was purged of air and heat was applied. When operating temperatures were reached (furnace generally 600° C), $TiCl_4$ was introduced into the boiler. After the reactor pressure had been elevated by $TiCl_4$ vapor, helium was bled off and sodium was added.

Feed rates were maintained as close as possible to 2 mol Na per 1 mol $TiCl_4$, and pressure in the reactor was held to a range of 0 to 2 lbf/in^2(ga). At the beginning of the reduction operation in a cool-top reactor, $TiCl_4$ vapor was introduced at the upper section of the reactor, and sodium was fed through the 0.021-in probe valve in a continuous fine stream. Because of the exothermic reaction, the melt temperature increased with increased feed rates. Since corrosion and contamination problems increased at higher temperatures, a maximum allowable melt temperature of 900° C was selected as the limiting factor in regulating the rates of feeding sodium and $TiCl_4$. Problems in operating the cool-top reactor included plugging of the sodium valves, sublimation of some $TiCl_3$, and condensation of a small amount of sodium on the reactor lid.

In the hot-top reactor, sodium was fed by increments at regular intervals through a 0.25-in needle valve. At the beginning of the reduction operation, tetrachloride vapor was introduced at the upper section of the reaction chamber. When the depth of the melt reached 3 or 4 in, the feed pipe was lowered and the tetrachloride vapor was discharged below the melt surface. The behavior of the pressure in the reactor and the melt temperature were very similar to those described for the cool-top reactor. The hot-top reactor prevented sublimation of $TiCl_3$ and condensation of sodium on the reactor lid, and less plugging of the sodium feed valve was experienced.

In operation of both cool-top and hot-top reactors, the heat of reaction generally raised the temperature inside the reactor to above that set for the furnace control, and heating from the furnace was required only to start the reaction. In the experimental work, the furnace temperature control was generally set at 600° C throughout the reduction operation to maintain the desired temperature if the reaction should be interrupted by plugging of the sodium valve.

Reductions in the 12-in-diam reactors were made with 14.5 lb of sodium and 60 lb of $TiCl_4$ to produce melts about 8 in deep. Feeding sodium and $TiCl_4$ generally took about 3 h to complete. The resultant melt then contained about 18 pct soluble titanium, and the AEV values ranged from 2.4 to 2.6. There was not much difference in composition of the melts produced in the cool-top and hot-top reactors.

At the completion of feeding sodium and $TiCl_4$, the melt contained an appreciable amount of $TiCl_3$, as indicated by the AEV values. Because the stoichiometric amounts of sodium and $TiCl_4$ to produce $TiCl_2$ were used, the presence of $TiCl_3$ in the melt was accompanied by the presence of metallic titanium. To convert as much as possible of the $TiCl_3$ and titanium present to $TiCl_2$, a postreaction soaking period was employed with the furnace temperature set to hold the melt at 650° C.

The effect of soaking on the melt product is shown in table 33. During the soaking, $TiCl_3$ and metallic titanium reacted to produce $TiCl_2$, as indicated by the general trend of increasing soluble titanium and the decreasing trend of the soluble titanium AEV.

The temperature at which the melts solidified ranged from 531° to 614° C, depending chiefly on the AEV of the soluble titanium as shown in table 34. Soaking decreased

Table 33.—Effect of soaking on the melt product

Soaking time, h	Run 1		Run 2		Run 3	
	Soluble Ti	AEV	Soluble Ti	AEV	Soluble Ti	AEV
COOL-TOP REACTOR						
0	17.5	2.46	18.8	2.36	18.4	2.64
3	18.9	2.33	18.9	2.30	20.0	2.59
6	18.9	2.26	19.1	2.28	20.0	2.23
9	19.3	2.25	19.3	2.25	20.1	2.20
12	19.4	2.21	19.3	2.25	20.2	2.20
15	19.4	2.18	19.5	2.23	NAp	NAp
18	19.8	2.15	NAp	NAp	NAp	NAp
HOT-TOP REACTOR						
0	17.8	2.42	18.0	2.57	NAp	NAp
3	18.6	2.41	18.7	2.48	18.5	2.25
6	19.2	2.29	18.9	2.43	18.8	2.12
9	19.6	2.27	19.2	2.39	18.8	2.13
12	19.7	2.24	19.3	2.34	19.2	2.14
15	19.8	2.22	19.5	2.30	19.3	2.14
18	NAp	NAp	19.6	2.28	19.3	2.11
20	NAp	NAp	20.0	2.24	NAp	NAp

AEV Average effective valence.
NAp Not applicable.

Table 34.—Solidification temperatures of the melt products

Melt	Soluble Ti		Solidification temperature, °C
	pct	AEV	
1	18.4	2.64	531
2	20.0	2.59	560
3	19.0	2.51	585
4	18.8	2.44	598
5	19.6	2.14	606
6	19.3	2.11	614

AEV Average effective valence.

the AEV of the soluble titanium and raised the solidification temperature of the melt.

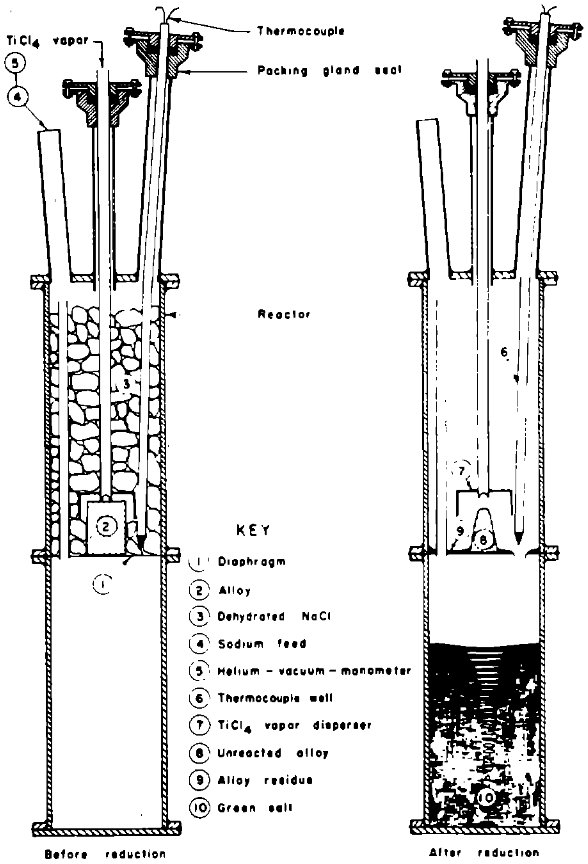

Figure 52.—Scrap alloy reactor.

Titanium Metal as a Reductant

Use of titanium metal as a reductant in the production of titanium lower chlorides (reaction 28) suggested a number of variations for producing a first-stage product for subsequent reduction to titanium metal. The presence of titanium metal during the partial reduction of $TiCl_4$ with sodium offered a means of decreasing the AEV of the reaction products as well as increasing the $TiCl_4$ content of the salt mixture. The use of titanium as a reductant also offered a method for recycling offgrade material produced in the second-stage reduction and a possibility for recycling scrap titanium.

The first experiments in which titanium was added to the reaction chamber were designed to determine the role of titanium as an agent for maintaining a low AEV during the reduction of $TiCl_4$ with sodium. For these tests, a shielded pipe weir was welded into the reactor diaphragm as shown in figure 52. Experiments were conducted in 16-, 19-, and 30-in-diam reactors. The melt, as produced by the reaction between $TiCl_4$ and sodium, came in contact with the titanium metal before it was discharged over the weir into the salt chamber below. The pipe weir was designed to give soaking to the product without requiring an additional soaking period. Samples taken of the various portions of the melt product indicated that salt from a position where it would be expected to solidify first, had a lower AEV value, i.e., a higher proportion of $TiCl_2$.

The reduction of $TiCl_4$ with titanium was further tested in a 16-in-diam simple diaphragm hot-top reactor. The titanium used was reject sponge, test bars, and buttons from magnesium reduction research. In a typical test, 80 lb of titanium was loaded to a depth of approximately 12 in on top of the diaphragm, and 90 lb of NaCl was placed on top.

The tetrachloride vapor feed pipe was lowered into the metal pile to about 2 in above the diaphragm. Although at a furnace temperature of 800° C, the temperature in the reactor was not high enough to melt the NaCl, the heat of the reaction and the lowering of the melting point when the $TiCl_4$ came into contact with the NaCl quickly rendered the salt molten. During most of the reduction operation, $TiCl_4$ vapor could be fed at a rate of about 50 lb/h with pressure in the reactor seldom over 3 lbf/in^2(ga). Toward the end of the operation, excessive pressure was frequently experienced and had to be reduced by occasional bleeding and reduction of the $TiCl_4$ feed rate. These conditions limited the practical concentration of titanium lower chlorides in the melt product to a maximum of about 30 pct soluble titanium.

When feeding of $TiCl_4$ was finished, the melt was held between 800° and 825° C for about 20 h to convert $TiCl_3$ to $TiCl_2$ and then was drained from the unreacted titanium metal into the salt chamber by puncturing the diaphragm. The reduction operation used 144 lb of $TiCl_4$ during a period of 3 h. The melt contained an average of 26.9 pct soluble titanium with an AEV of about 2.19 and had a solidification point of 722° C. Inspection of the unreacted titanium indicated that all shapes of the metal were consumed about equally. Altogether, about 45 pct of the scrap metal was reacted.

Titanium Alloy Reductions

Much of the scrap generated in processing titanium is in the form of alloys containing aluminum, tin, vanadium, chromium, zirconium, molybdenum, manganese, and other alloying elements. Eight alloys were tested to determine their amenability as reductant for $TiCl_4$ in the formation of titanium lower chlorides. Four of the alloys were common commercial alloys, and four were synthetic mixtures prepared for alloy recycling studies. The nominal and actual compositions of the alloys are shown in table 35. The tests were conducted in a 6-in-diam reactor of the type shown in figure 52.

Table 35.—Composition of test alloys, percent

Alloy number	Nominal composition	Chemical analysis							
		Al	Cr	Cu	Mn	Mo	Sn	V	Zr
1	8 Al, 3 Mo, 1 V	8.00	ND	ND	ND	1.25	ND	1.11	ND
2	5 Al, 2.5 Sn	5.06	ND	ND	ND	ND	2.50	ND	ND
3	4 Al, 3 Mo, 1 V	5.52	ND	ND	ND	2.52	ND	.90	ND
4	6 Al, 4 V	6.17	ND	ND	ND	ND	ND	4.21	ND
5	2.5 Mo, 2.5 Mn	ND	ND	ND	2.64	2.55	ND	ND	ND
6	2.5 Cr, 2.5 V	ND	2.86	ND	ND	ND	ND	2.45	ND
7	2.5 Zr, 2.5 Mn	ND	ND	ND	2.92	ND	ND	ND	2.31
8	75 Cu	ND	ND	71.39	ND	ND	ND	ND	ND

ND Not determined.

In a typical reduction, about 2 lb of the alloy was placed on the diaphragm, and the $TiCl_4$ feed pipe was installed with the discharge directly over the alloy. Ten pounds of sodium chloride, in the form of lumps, was then loaded on the diaphragm. The furnace temperature was set at 700° C. The tetrachloride feed rates varied with the different alloys depending on the reaction rate of the alloys with the tetrachloride. A soaking time of 24 h at 700° C was employed.

Operating data and analysis of the melts and residual alloys after leaching are shown in table 36. The alloy utilization was calculated from the weight of the leached residual alloy and the weight charged. Most of the residues had an insoluble crust that contained increased proportions of alloying metals. The residues also contained iron, chromium, and nickel from corrosion of the reactor surfaces. Thus, titanium utilization was greater than shown by the calculations, especially for alloy 8, the 75-pct copper alloy, which had a thick layer of copper on the surface.

Table 36.—Operating data and analysis—alloy reductions

Alloy	Alloy form	Reaction time, h	Alloy utilization, pct	Melt AEV
1	Rod, 2-in-diam	9.0	52.0	2.61
2	Plate, 3/16-in	3.4	62.6	2.60
3	Sheet, 12-ga	1.3	74.0	2.52
4	Bar, 2- by 2-in	5.3	49.2	2.58
5	Ingot	8.0	49.7	2.80
6	do	9.5	49.6	2.84
7	do	7.3	54.3	2.76
8	do	24.3	29.3	2.87

Alloy	Melt analysis, pct									
	Al	Cr	Cu	Fe	Mn	Mo	Ni	Sn	V	Zr
1	0.56	0.11	ND	0.15	0.05	<0.01	NA	0.02	0.10	0.04
2	.28	.04	ND	.01	ND	<.01	NA	<.01	<.01	ND
3	.22	<.01	ND	.01	.01	<.01	NA	<.01	<.01	ND
4	.29	.02	ND	.05	ND	<.01	NA	<.01	ND	ND
5	.07	.12	0.01	.02	.19	<.01	NA	<.01	.02	ND
6	.05	.20	.01	.17	.03	.01	NA	ND	.06	.02
7	ND	.18	ND	.84	.16	ND	NA	.03	.06	.12
8	.06	.29	.30	.67	.01	.01	NA	.01	.04	ND

Alloy	Residue analysis, pct									
	Al	Cr	Cu	Fe	Mn	Mo	Ni	Sn	V	Zr
1	2.91	3.41	0.01	45.69	0.05	4.53	0.15	0.04	2.51	ND
2	6.82	.14	ND	22.32	ND	.02	ND	18.63	.41	ND
3	11.43	.68	.13	4.40	ND	19.00	<.01	<.01	3.70	ND
4	3.81	4.66	.08	49.01	ND	<.01	ND	.08	10.64	ND
5	.15	4.93	.20	47.57	.01	10.56	.58	.03	.88	0.06
6	.10	9.77	.08	50.73	.01	.13	.30	ND	5.85	.17
7	ND	3.90	ND	64.43	.07	ND	.25	.05	.24	.08
8	.06	<.01	90.61	.67	<.01	ND	ND	.10	.13	ND

AEV Average effective valence.
NA Not analyzed.
ND Not determined.

A reduction was also made in a 12-in-diam reactor in which approximately 2 lb of each of the alloys and the titanium buttons were charged into the reactor diaphragm. Alloy 8 was added as minus 3-mesh granules instead of ingot to promote the reaction of this alloy. In this procedure, each alloy was subjected to the same treatment for the same time period. Alloy utilization varied from 29.8 to 100 pct. Utilization of the high-copper alloy was not calculated because the recovered pieces appeared to be almost pure copper. The melt had an AEV of 2.6 after a 50-h soaking period and contained 25.8 pct soluble Ti, 0.29 pct Al, 0.01 pct Cu, 0.05 pct Mn, 0.03 pct V, 0.01 pct Zr, and less than 0.01 pct Cr, Fe, Mb, and Sn.

Analysis of the melt products indicated that recycling of titanium alloy scrap by reaction with $TiCl_4$ was not feasible unless a lower AEV melt could be produced and methods developed either for preventing solution of the alloying elements or for removing them from the melt.

Purification of Lower Chloride Melts

The increased impurity content of the melts obtained when titanium alloys were used as reductants was attributed not only to the increase in content of the impurity elements in the system but also to the high AEV of the melts. The high AEV indicated the presence of a high proportion of $TiCl_3$, which was very corrosive to materials of construction in the reactor system.

The melt product from reduction with alloy 1 was filtered through a micromatic, stainless steel filter with a mean pore size of 20 µm to determine whether the impurities were in solution or suspension. The filter reduced the iron content from 0.15 to 0.01 pct, but did not appreciably reduce other impurities.

Reductions with sodium or titanium sponge or combinations of these two reductants produced lower chloride melts with AEV's of 2.2 to 2.3 and no metallic impurities greater than 0.01 pct. Titanium sponge was added to the melts obtained from the reductions using titanium alloys, and the melts were soaked for an additional 24 h at 750° C. The AEV was reduced to 2.2 or 2.3 and the chromium, copper, iron, molybdenum, and vanadium contents were reduced to less than 0.01 pct. Aluminum, manganese, and zirconium, however, remained in the melts.

Titanium and TiO_2 were added to one of the melts to convert the aluminum to alumina, according to the overall reaction:

$$3TiO_2 + 3Ti + 4AlCl_3 \rightarrow 6TiCl_2 + 2Al_2O_3. \quad (31)$$

The melt was divided into two fractions; one was soaked for 24 h at 750° C with the addition of TiO_2 and titanium sponge and the other was soaked with the addition of TiO_2 only. The results, shown in table 37, demonstrate that TiO_2 in combination with titanium

Table 37.—Analysis of melt before and after soaking with TiO_2

Melt description	AEV	Soluble Ti, pct	Al, pct
Before treatment	2.32	16.83	0.03
Soak with TiO_2 and Ti	2.18	17.14	.01
Soak with TiO_2	2.37	15.37	.03

AEV Average effective valence.

metal will precipitate aluminum from a lower chloride melt.

A similar test was made on a melt containing manganese and zirconium. The zirconium was removed, but the manganese was not. No method was discovered that would remove manganese from the lower chloride melts.

Reduction of Titanium Lower Chlorides (95)

Equipment

The second stage of the two-stage reduction of $TiCl_4$ (reaction 25) was conducted in reactors similar or identical to those used for making the first-stage reductions. Tests were made in one-, two-, and three-compartment reactors. When three-compartment reactors, shown in figure 53, were used, the top compartment was used for the first-stage reduction, the middle compartment for the second-stage reduction, and the lower compartment to receive the barren salt. A sampling chamber was attached to the side of the middle chamber to provide a sample of the first-stage product. Single-compartment reactors equipped with 20-ga mild steel removable liners were used for the partial reductions so that the reaction mass could be removed in one piece for observation.

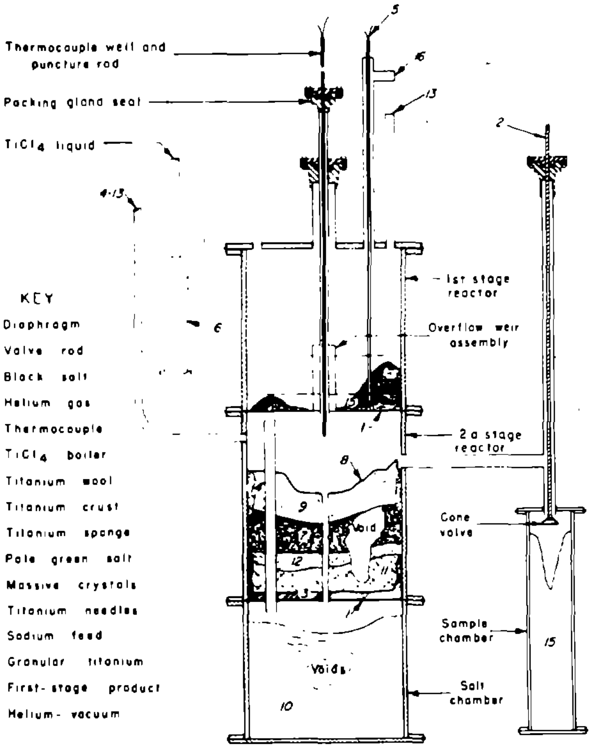

Figure 53.—Two-stage reactor showing products from a typical reduction.

Experimental Procedures and Results

Titanium lower chloride melts were made by the procedures described previously. The melts were soaked for 20 to 25 h at 750° C. The AEV was 2.2 to 2.3.

In the second stage, molten sodium was added to the surface of the melt because all attempts to feed below the surface resulted in clogging of the feed pipe with titanium metal and NaCl.

Two reduction methods were employed, designated as high- and low-temperature techniques. The high-temperature technique consisted of feeding molten sodium, in increments, to the surface of first-stage melts maintained above 800° C. Reaction started at the melt surface and raised the melt temperature with the first sodium addition. The rate of feed at the start of the reduction was very slow until a layer of NaCl had formed. In the low-temperature method, all of the sodium was usually fed to a solidified first-stage melt, and the temperature was increased gradually until the reaction started at about 600° C. The solidified melt had a shrinkage space of $\frac{1}{16}$ in at the reactor wall and a center void near the top surface. Molten sodium would penetrate the openings, and the initial second-stage reaction occurred around the outside surface of the first-stage product and in the center void. The heat generated by the reaction melted the first-stage product.

Products of Reduction

The titanium metal produced by the second-stage reduction was heterogeneous in form, not only from one reduction to another, but within the same reduction. Titanium was formed as powder in the black salt, as metal foil in a spongy, crumpled configuration, as small granules, usually sintered into a spongy formation, as a fine filamentary wool, as titanium needles of varying size, and as crystals in various shapes and sizes. All of the forms were present in varying proportions in practically every reduction.

The black salt consisted of fine titanium particles dispersed in NaCl. The particles of metal trapped the salt so that it would not drain from the metal. The black salt was always located adjacent to the metal surfaces of the reactor equipment. The titanium recovered from the black salt by leaching was of poor quality; the hardness varied from 225 to 235 HB, and the impurity content was high.

The metal foil and spongy formation, which was composed of small granules, appeared to form in the areas where the sodium first contacted the lower chloride melt. The formations of filamentary wool, needles, or crystals were located beneath, but adjacent to, the granules. The purity of the metal product improved as the size of the metal form increased. Large crystals, up to 1 in. in maximum dimension, had hardnesses as low as 50 HB.

The salt drained from the second-stage reduction was essentially NaCl containing a small quantity of unreacted lower chlorides. The color of the salt varied from white to light green. In most of the tests in which good quality metal was obtained, the tapped salt contained 1 to 2 pct soluble titanium with an AEV below 2.1.

Comparison of High- and Low-Temperature Reductions

The results of tests using high- and low-temperature reduction techniques are compared in table 38. The most consistent results and the best quality products were obtained using the low-temperature technique. The lowest hardness metal was obtained from the reaction that produced the coarsest crystalline titanium (reduction 5, table 38).

Table 38.—Comparison and reproducibility of high- and low-temperature reduction techniques

Reduction	Melt temp range, °C	Titanium metal produced					
		Lowest HB	80 HB or less, pct	Av HB[1]	Minus 65-mesh metal, pct	Separated crystals	
						All metal recovered,[2] pct	Av calculated HB
		HIGH-TEMPERATURE REDUCTION TECHNIQUE					
1	[3]865-945	62	13.7	160.0	11.6	[4]26.0	83
2	[3]810-927	63	1.8	110.8	4.6	[4]38.6	89
3	[3]850-992	110	0	166.2	7.6	[5]49.8	113
		LOW-TEMPERATURE REDUCTION TECHNIQUE					
4	522-882	73	17.1	87.9	11.2	[6]36.3	85
5	396-854	55	27.5	87.6	10.9	[6]44.2	74
6	586-818	71	17.1	131.4	10.8	[6]32.8	83

[1] After removing minus 65-mesh metal and black salt.
[2] Including minus 65-mesh metal and black salt titanium.
[3] After sodium was added.
[4] Mixture of short needles and granular crystals.
[5] Short, fine needles.
[6] Massive Ti crystals (blocky hexagons, lamellar plates, twins).

Partial Reduction Tests

Four second-stage reductions were made in which 10, 25, 50, and 75 pct of the stoichiometric quantity of sodium was added. These tests were designed to determine the progress of the formation of titanium metal in the lower chloride melts. The high-temperature reduction technique was employed in single-compartment reactors. Sodium was added in increments to a first-stage melt, 12 in. in diam and 8 in deep. After reaction periods of 0.8, 1.4, 2.6, and 3.5 h, respectively, the reactor was slowly cooled. The melts were removed in one piece and split vertically for observation before leaching for metal recovery.

The average hardness of the recovered metal decreased as the percent sodium addition increased, indicating that purer titanium formed as the reaction proceeded. Inspection of the melt sections showed that fine titanium granules bridged across the melt surface, and crystal growth advanced downward as the reduction progressed. Titanium needle growth appeared below the porous granular titanium in the 10-pct Na addition, and the more massive and purer titanium crystals appeared below the porous barrier and increased in quantity as the proportion of sodium increased. Void areas were observed below the massive titanium crystal formations. No titanium metal settled to the bottom or built up on the walls except in the 75-pct Na addition. Black salt did not appear until the 75-pct Na addition. A pale blue-green salt embedded the metal products. In all of the tests, the dark green salt beneath the titanium formation retained practically the composition of the first-stage reduction melt.

Agitation During Reduction

Tests were made using helium or argon for agitating the melt during the second-stage reduction to determine the effect on titanium crystal growth. Gas was bubbled through the melt during and after the addition of sodium. The starting melts contained 19.1 pct soluble titanium with an AEV of 2.25.

The metal in reductions using either helium or argon was observed to be chiefly in the top half of the product cake and consisted of fine titanium granules and short needles compacted and sintered together in layers with a thin gray titanium foil separating the layers. Small voids occurred in the layers, especially where agitation of the melt with helium was employed. The 0.25- and 0.5-in-diam voids were lined with bright, silvery titanium foil.

Agitation with inert gas caused sodium vapor to condense and freeze in pressure-release lines and valves. Agitation during the second-stage reduction was more conducive to the formation of titanium sponge than of titanium crystals.

Reduction of Melts Containing Various Percentages of Soluble Titanium

First-stage melts were prepared in which the soluble titanium content was varied from 4.5 to 27 pct. The low-temperature technique was used for making second-stage reductions. After the reductions were completed and the reactors were opened, the products were inspected, separated, and leached. Table 39 gives starting melt and product data for these tests.

Table 39.—Starting melt and product data for melts with variable soluble-titanium content

Reduction	Starting melt		AEV	Metal product		
	Soluble Ti, pct	Solidification temp, °C		Minus 65-mesh, pct	Crystals, pct	Calculated hardness, plus 65-mesh, HB
1	4.5	781	2.11	14	0	249
2	9.7	783	2.13	7	22	174
3	14.7	673	2.30	17	22	127
4	19.7	599	2.13	28	44	88
5	[1]27.0	721	ND	17	30	121

AEV Average effective valence.
ND Not determined.
[1] Calculated value, sample not taken.

About 90 pct of the titanium metal obtained from the reduction of a 5-pct soluble titanium melt consisted of very fine particles sintered together into a delicate filamentary growth. The filaments were interlaced to give a soft spongy mass after removal of the salt by leaching.

The metal from the reduction of a 10-pct soluble titanium melt was formed mostly in the black salt and in fine granular crystals sintered into spongy masses that adhered to the liner and thermocouple well. A small quantity of massive titanium crystals was found in the black salt.

The product from the melt containing 15 pct soluble titanium was similar to the product from the melts containing 5 and 10 pct soluble titanium, except that a larger deposit of sintered granular crystals adhered to the thermocouple well. Also, a growth of tabular crystals was observed between the granular crystals on the thermocouple well and the black salt on the bottom.

The product formation after the reduction of 20 and 27 pct soluble titanium melts was quite similar except that the titanium crystals from the 27-pct melt were larger, thicker, and were present in greater quantity. The crystals were of various types including lamellar plates and blocky hexagonal crystals with much twinning apparent.

The black salt was always present on the bottom and lower wall of the reactor. Also, a granular form of crystalline titanium appeared to grow out from the thermocouple well and reactor walls, and more massive crystals were observed in the void areas between granular or needlelike metal and black salt. The larger crystals extended either from the porous metal above or from the black salt.

Effect of Reduction Melt Depth and Reactor Diameter

Reduction of titanium lower chlorides using the low-temperature reduction technique on melts 8 and 12 in deep yielded a higher proportion of separable crystals and larger crystals for the 12-in depth. The proportion of minus 65-mesh fines was also lower from the 12-in-deep melts.

Tests in which the diameter of the reactor was increased from 12 to 19 in yielded larger and more massive crystals as the diameter increased. The proportion of black salt decreased as the diameter of the reactor was increased.

The most salient information obtained from varying the depth of first-stage melts and reactor diameters was that as the volume of the starting melt increased, the proportion of titanium recovered as separate crystals and the average size of the crystals increased. Also, a lower proportion of black salt was formed in the larger volume melts.

Figure 54 shows the crystal formation in a 19-in-diam reactor after reduction of a 12-in-deep melt. The diaphragm was removed to expose the growth of massive crystals immediately above the diaphragm. Crystals can also be seen extending from the black salt on the diaphragm (lower left corner) and on the reactor walls. Figures 55 and 56 show various shapes and sizes of individual crystals. The massive crystalline titanium was in the form of lamellar plates, truncated pyramids, bipyramids, prisms with one end chisel pointed, and twins of lamellar plates or truncated pyramids. In some cases, the crystals consisted of several parallel plates separated by wirelike columns, or were built up of plates with parallel crystal faces.

Recycle of Fines and Offgrade Metal

In the second-stage reduction, the minus 65-mesh metal (including black salt) represented from 10 to 30 pct of all the titanium produced. This fine material was of poor quality as shown by high hardness, 160 to 400 HB, and high iron content, 0.1 to 2.5 pct. The fine titanium obtained by screening of the leached metal and the black salt product could be recycled through the first-stage reactor and allowed to react with $TiCl_4$ to produce $TiCl_2$ according to reaction 28.

Recycle tests were made in a 19-in-diam, three-chamber reactor. In these tests, the fine metal from second-stage sodium reductions and, in some cases, additional offgrade sponge from magnesium reductions, were placed on a diaphragm of the first-stage reaction compartment. Sodium metal and $TiCl_4$ were then fed into the compartment to form lower titanium chlorides and NaCl. Additional $TiCl_4$ was fed into the chamber in a quantity to react with a predetermined proportion of the titanium metal placed on the diaphragm.

After a soaking period for the first-stage reaction product, the melt was drained into the second-stage reaction compartment by puncturing the diaphragm. The melt was cooled to its solidification temperature, and the low-temperature technique was used to produce metal in a second-stage reduction. The titanium from a typical test had a calculated average hardness of 88 HB after removing the minus 65-mesh fraction and the titanium in the black salt. Ten percent of the metal product had a hardness of 60 HB.

VAPOR-PHASE REDUCTIONS

Experiments with the reductant and the titanium chloride in the vapor phase were concerned with two reduction techniques; the first was the reaction of sodium vapor and $TiCl_4$ in the presence of titanium sponge and the second, the reaction of sodium vapor and sublimed $TiCl_4$, also in the presence of titanium sponge. The sponge was sintered lumps of titanium (minus 1 plus 3 mesh) from two-stage sodium reductions.

Reduction of Titanium Tetrachloride

Preliminary tests in 6-in-diam reactors showed that in the presence of sodium and $TiCl_4$ vapors, titanium metal would grow on the surface of titanium sponge. The metal was in stalagmitic formations on the sponge rather than in the desired massive crystalline form. The growths were composed of fine titanium granules sintered together and coated with a skin of sintered titanium powder. The stalagmites were easily broken loose from the sponge. Best results were obtained when the reactor was under a partial vacuum, and the reaction zone temperature was above the melting point of NaCl.

A reactor assembly with a 12-in-diam by 30-in-long reaction chamber was constructed as shown in figure 57 to determine the feasibility of a continuous vapor-phase reduction operation. Major features of the assembly were a sodium boiler surrounding the reaction chamber, a perforated wall basket inside the reaction chamber that held a concentric 1-in-thick layer of sponge, a cutter for removing titanium growths from the surface of the wall basket, and separate titanium metal and salt chambers below the reaction zone to collect the reaction products. The upper 18 in of the reactor wall was perforated with 0.375-in holes spaced 1.5 in apart and sloped toward the bottom of the reactor to provide for sodium vapor flow through the sponge and to prevent salt products from draining into the sodium boiler. The shaft of the cutter extended through a packing gland in the center of the lid and could be lowered and rotated to shear titanium from the surface of the wall basket. A flapper valve was provided to divert products to either the metal chamber or the salt chamber, as desired during different periods of the operating cycle. A salt drainage shelf was welded to the reactor wall below the basket and above the titanium metal chamber to drain the salt products into the salt chamber.

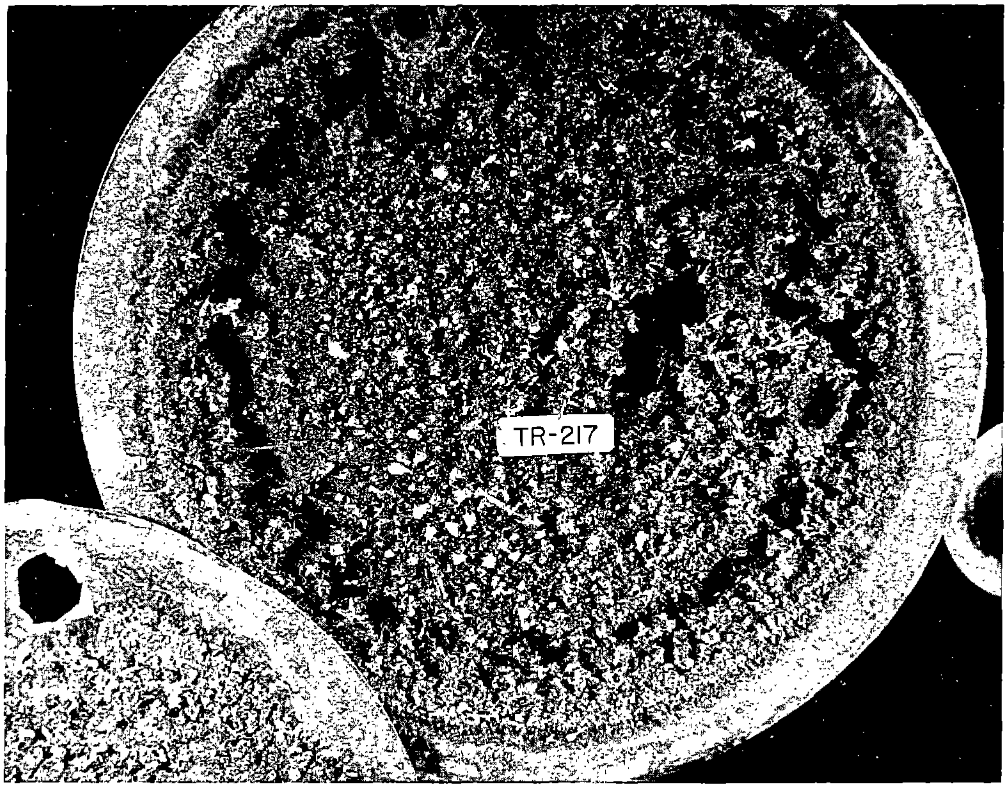

Figure 54.—Titanium crystal formation in 19-in-diam crucible.

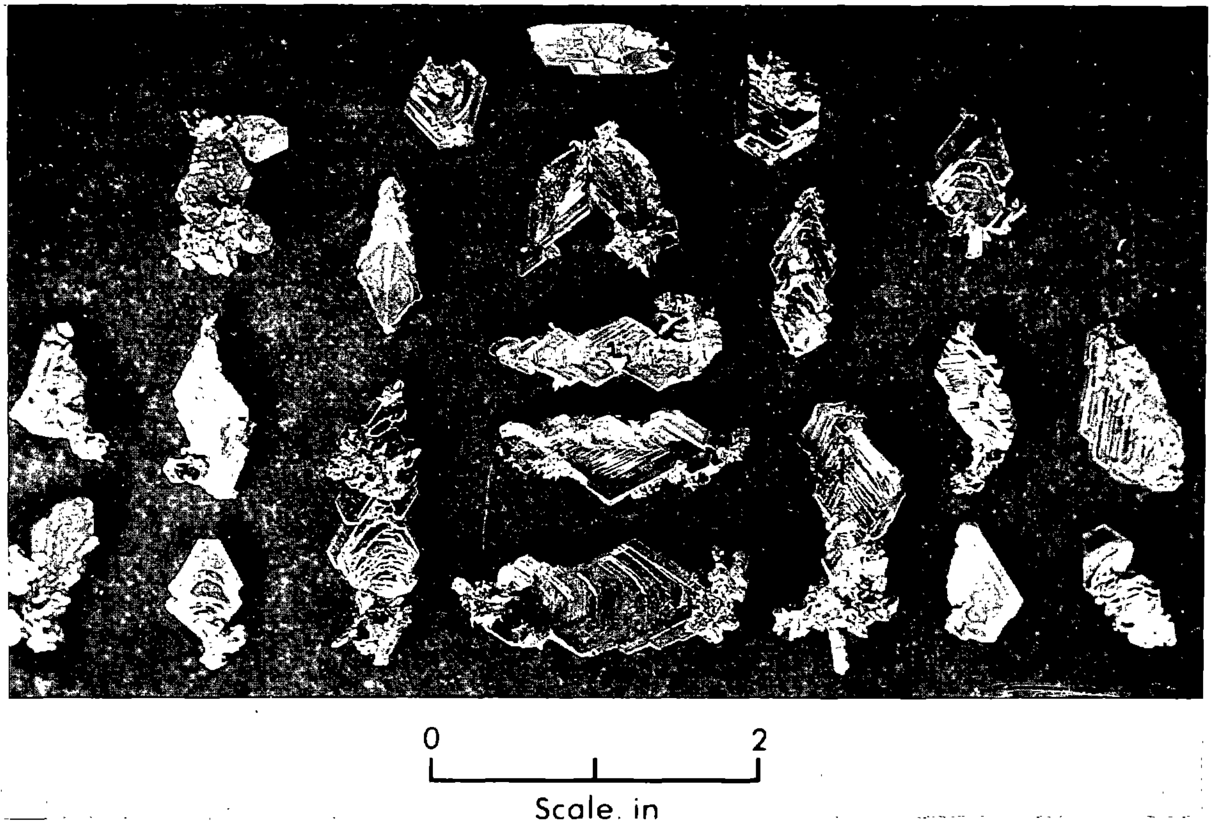

Figure 55.—Lamellar titanium crystals, Brinell hardness number less than 54.

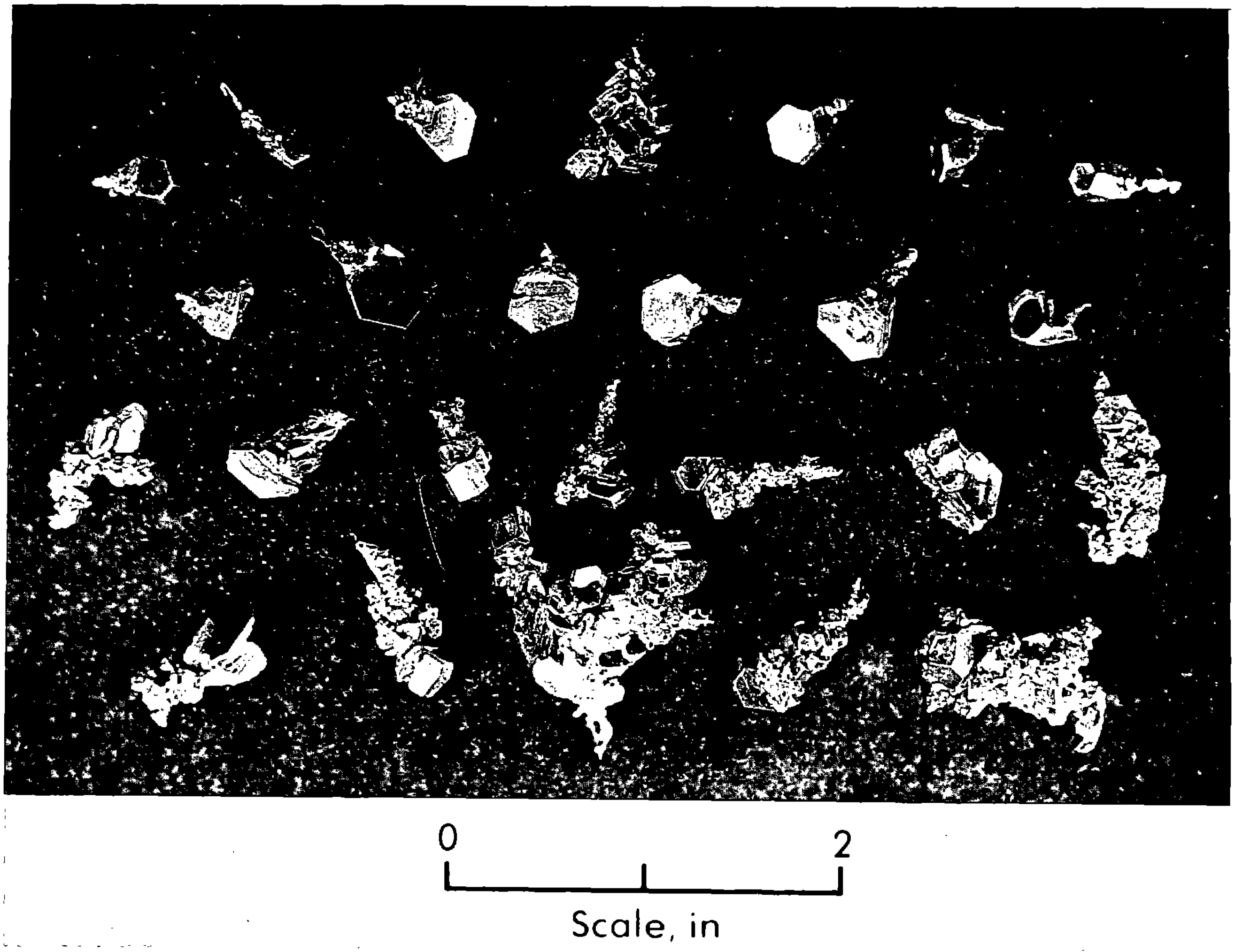

Figure 56.—Blocky hexagonal titanium crystals.

Operation of the reactor was started at 800° C after evacuation to a pressure of 12 in Hg. Sodium was fed to the boiler intermittently in 2-lb increments. The $TiCl_4$ feed rate was regulated to maintain a slight pressure differential between the sodium vaporizer and the reactor, and varied between 0 and 30 cm^3/min. The cutter was operated during periods when all of the sodium in the vaporizer had been utilized. A sight glass in the lid indicated when the wall growth could be removed. Before operation of the cutter, the reactor was pressurized with helium, and the flapper valve was tilted to cover the salt compartment. After operation of the cutter, the equipment was repositioned and a new cycle was started.

At the conclusion of a five-cycle campaign during which 24 lb of sodium and 49.5 lb of $TiCl_4$ were added, the reactor was opened, and metal growths and salt products were observed. The titanium formations appeared to grow not only on the sponge through the holes in the basket but also on the surface of the basket, which was covered with a thin surface of sintered titanium. Many of the openings in the basket were sealed over with titanium metal. Only 3.5 pct of the titanium added as $TiCl_4$ was recovered from the metal chamber, and a part of this was produced by a second-stage reaction of green salt and sodium vapor. About 3 pct had been cut from the basket but had lodged on the salt drainage shelf, to which it had sintered so tightly that chiseling was required to remove it. About 70 pct of the titanium added as $TiCl_4$ was in titanium lower chlorides in green salt and as metal adhering to reactor surfaces. The balance was in the sponge in the wall basket and as a second-stage reaction product in the salt chamber. Ropelike crystal formations, hollow in the center and covered with a sheath of sintered titanium powder, grew on the reactor surfaces. The hardness of metal from the vapor-phase reactor varied from 226 to 353 HB.

The vapor phase reduction of $TiCl_4$ appeared impractical because the fine titanium powder coated the reactor assembly and sintered into a solid sheet that rapidly thickened to freeze all moving parts. The usual problem of lower chloride formation was similar to that encountered in liquid-phase reductions. In addition, the operation was difficult because of the requirement for maintaining a pressure differential between the sodium vaporizer and the reactor.

Reduction of Titanium Trichloride

Tests were conducted to investigate the characteristics of reduction of $TiCl_3$ sublimates with sodium vapor in the presence of titanium sponge. Sublimation tests on high AEV titanium chloride-sodium chloride melts in a vertical sublimer yielded condensates containing 93 pct $TiCl_3$ and 7 pct NaCl.

A reactor was designed that provided separate vaporizing chambers for sodium and for a high-AEV melt. It was constructed so that the sodium and $TiCl_3$ could react on the surface of titanium sponge, and the salt product from the reduction could drain from the sponge through a perforated plate that supported the sponge above a salt chamber.

Results showed that only 2.5 pct of the titanium produced had grown on the sponge. The same problems were encountered as in the reaction of $TiCl_4$ and sodium vapor. Additional problems were corrosion and plugging of pipes by condensed sublimates.

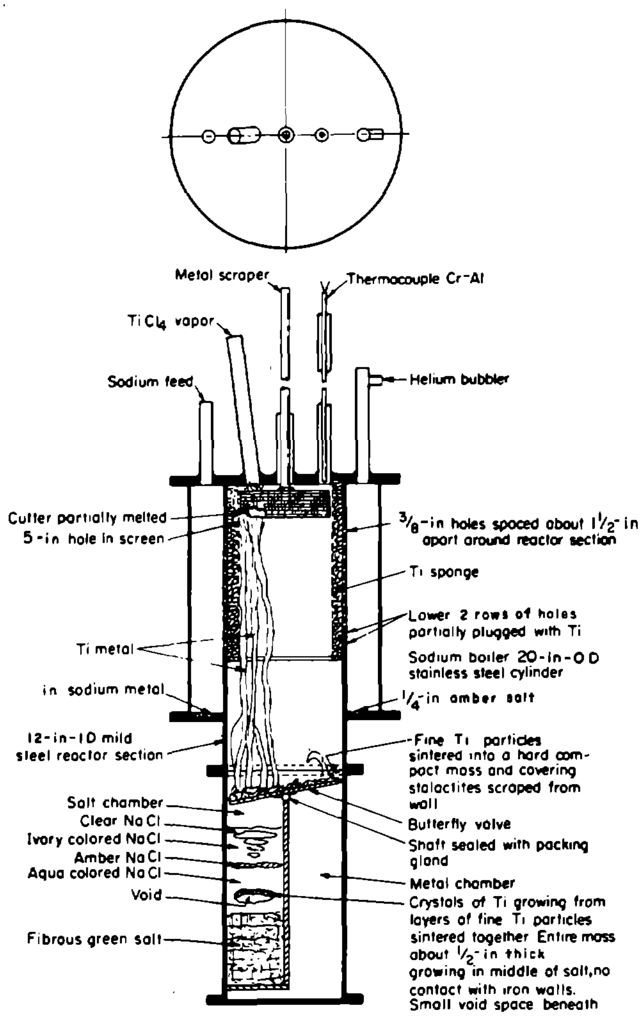

Figure 57.—Vapor-phase reactor showing deposition of products.

SUMMARY

High-purity titanium metal was produced by reduction of titanium chlorides with sodium metal. Best results were achieved by reducing $TiCl_4$ in two stages: first to $TiCl_2$, then to the metal. The reduction product contained titanium in crystalline and amorphous forms; only the crystalline material was of acceptable purity. Titanium scrap metal and alloy containing chromium, copper, iron, molybdenum, vanadium, aluminum, and zirconium was purified by reaction with $TiCl_4$ to form $TiCl_2$ followed by reduction with sodium. Alloys containing manganese could not be purified because manganese could not be eliminated from the melt.

CHAPTER 7.—MELTING AS A PURIFICATION STEP

EARLY DEVELOPMENTS

It was recognized early in the development of titanium metallurgy that sponge is not suitable for fabrication of titanium sheet, rod, plate, and hardware. Useful titanium products must possess acceptable homogeneity, microstructure, physical properties, and purity. Residual chloride in Kroll process titanium sponge must be reduced to very low levels to allow satisfactory welding to be performed. Melting is currently the only known procedure for reducing the chloride left in the sponge after distillation or leaching to an acceptable level.

The earliest work on melting of refractory metals such as titanium was conducted by Von Bolton in 1909 (*212*). The groundwork of modern melting technology was laid by Kroll in the early 1940's (*112*). Other important contributions were made by Park and Ham (*158*) and the work reported by the Office of Naval Research (*187*).

BUREAU OF MINES DEVELOPMENTS

The rapid development of the titanium industry of today has been made possible by the continuously improved and newly developed methods and techniques involved in producing the metal and consolidating it to a usable form. Titanium has many chemical characteristics that make it difficult to melt the metal for producing ingots and yet retain the high degree of purity required. The purity of the base metal and the cleanliness of the melting and fabricating processes play important roles in developing alloys with optimum ductility and toughness in the final wrought form.

Contamination from the atmosphere, from adsorbed and occluded water, and from refractory materials presents difficult problems to the melter.

Numerous investigations of refractories for containers in melting titanium have been made by Kroll (*114*), Brace (*25*), Eastwood and Craighead (*47*), March and Scholes (*131*), and others. All results indicate some degree of reaction and resultant contamination. The use of refractories as containers for molten titanium does not appear to be feasible. Carbon or graphite has been used as a crucible material for induction melting of titanium; however, the pickup of carbon during melting is sufficient to cause a serious loss of bend ductility and toughness.

To circumvent the difficulties arising from the reaction of molten titanium with refractories and air, several types of inert-atmosphere arc-melting furnaces have been developed for laboratory research and production uses (*117, 187*).

One of the first successful melting methods involves feeding titanium sponge into a water-cooled copper crucible in which a tungsten-tipped or graphite electrode maintains a direct-current arc to the molten pool. As the ingot is built up vertically the electrode is raised. The molten titanium does not wet the copper, and only a small portion of the ingot is maintained in the molten state. An inert-gas atmosphere of argon and helium provides atmospheric protection.

The work of the Bureau of Mines in zirconium metallurgy led to development of an inert-atmosphere consumable-electrode arc furnace (*192*), similar in some respects to arc furnaces used for melting molybdenum. A continuously formed electrode with a regular cross section was fed through drive rolls and water-cooled copper power rolls. With this arrangement only a relatively short length of electrode was required to carry the heavy currents used in melting. The voltage drop in the electrode from the power rolls to the arc did not affect the operation, even with the change in length that occurred as the ingot was built up in the water-cooled copper crucible.

Consumable-electrode arc melting is now accepted throughout the industry as the best method for producing ingots of zirconium, titanium, molybdenum, and their alloys. In addition, the technique is widely used in laboratories for fusing samples of such metals as hafnium, chromium, tantalum, columbium, and thorium. The production of consumable electrodes from these metals presents some rather difficult problems, the accepted industrial solution being the use of heavy-powder metallurgy-type presses. The Bureau of Mines has added considerably to the knowledge of this process (*17-18, 65, 116, 192*).

The consumable-electrode arc-melting furnace consists esentially of a controlled atmosphere or vacuum chamber water-cooled copper cup and an electrode made of the metal to be melted. The electrode is heated by an electric arc drawn from it to a charge of the same material in the copper cup, and this causes melting and dripping. The molten material is collected in the water-cooled cup where the lower layer quickly solidifies. As the electrode melts, a molten pool is maintained at the top of the ingot by liquid falling from the electrode, while a comparable amount of material is solidifying at the bottom and sides of the pool. Thus only a portion of the heat is molten at any given time.

The electrode itself is often of square or circular cross section, of from 1 to several inches in diameter and initially perhaps 2 to 6 ft long. It must have moderate mechanical strength and reasonably uniform electrical conductivity. Contamination should be minimized throughout the fabrication process.

The following principal fabricating processes were studied by the Bureau of Mines:

1. Pressing sponge or crushed chips into briquets.
2. Electrical sintering, in lieu of more intense pressing, of short stacks of briquets that were formed under low pressure.
3. Jointing briquets by spot welding or by strip welding.
4. Assembling electrodes directly from massive scrap by welding.
5. Nippling, in which ingots produced in a small furnace are joined for use as the consumable electrode in a larger furnace.

A 1968 Bureau bulletin by Beall summarizes most of the Bureau's efforts in the development of consumable electrode vacuum arc melting (*19*).

RECENT DEVELOPMENTS

A 1981 publicaton by Pridgeon (*167*) brings up to date the principles and practices of both vacuum induction melting and vacuum arc remelting.

A new innovation in the refractory metal melting has been developed by the Bureau (*30*). Induction slag melting is an induction melting process utilizing a segmented, water-cooled copper crucible. The crucible is segmented to prevent attenuation of the field of the induction coil, and a salt, such as CaF_2, is added to the crucible during melting to electrically insulate the crucible segments from the molten metal. This melting technique was developed by the Bureau as a means of consolidating reactive metal scrap as part of its goal of effective recovery of secondary metals.

In 1967, the titanium industry was concerned with prospects of large quantities of titanium scrap being generated by such projects as the supersonic transport. For this scrap to be recycled conveniently, a method was needed for consolidating the loose scrap into electrodes for remelting in consumable electrode arc furnaces used by the titanium industry. Induction slag melting was developed by the Bureau for this purpose, and other scrap melting processes were developed by industry at about the same time. Processes considered by industry for scrap melting included nonconsumable electrode arc melting, electron beam melting, and plasma melting.

The anticipated titanium scrap surplus did not develop because of cancellation of programs, a decline in the titanium market, and competition for the titanium scrap for other uses. Interest in these alternative melting processes has continued, however, as a means of reducing the cost of titanium through more effective utilization of available scrap.

The Bureau's work on induction slag melting has also continued because of increasing interest in the process for melting a variety of materials other than titanium scrap. The process is particularly useful for melting reactive metals that are difficult to fabricate into consumable electrodes but must be melted in water-cooled copper crucibles. Examples of other materials that have been melted in studies include reactive metal sponge, simulated radioactive nuclear scrap, and metals such as cobalt and chromium.

Calcium fluoride and mixtures of CaF_2 and MgF_2 have been used exclusively as the salt for induction slag melting. The choice of CaF_2 and MgF_2 was based on results of studies on electroslag melting of reactive metals conducted by the Bureau.

Still another process, electroslag melting, has seen a linear growth in total metal melting, from 100,000 to 500,000 st in the period 1960 to 1970. It has been successfully aplied to refractory metals such as titanium. A comprehensive Bureau bulletin by Nafziger (*141*) covers the historical development of this process and the Bureau's contribution to its success.

The electroslag process is a secondary melting technique developed several decades ago, which can be used for a variety of metals and alloys, provided appropriate fluxes and melting parameters are employed.

The electrode is usually consumable and is composed of the metal or alloy to be melted. It may be pressed sponge or scrap, or it may be cast or wrought material. Usually, minimal electrode preparation such as descaling or surface dressing is required. The diameter of the electrode is smaller than that of the crucible, although the ratio can vary within relatively wide limits. As practiced in the laboratory, a threaded stub of the same metal or alloy to be melted is welded to the top of the electrode and attached to a movable water-cooled copper electrode support. This in turn is connected to the power supply, which may be either single-phase ac, dc straight polarity (negative), or dc reverse polarity (positive). Three-phase may also be used wherein three electrodes are used.

Before starting, a base plate and/or turnings of the metal or alloy to be melted are placed in the bottom of a water-cooled cupper crucible. This crucible is fitted with a flange on top, to which the second power lead is connected.

Present practice calls for charging all or a portion of the dry, prefused flux into the bottom of the crucible around the electrode prior to initiation of the melt.

Additional flux may be charged during the melt through the top of the furnace if an air melt it being conducted, or through a side feeder during a closed-furnace melt.

At the beginning of a melt, an arc is struck between the electrode and the base plate. This is rapidly quenched by the fusing flux. As soon as the flux has completely fused, the power is increased, the temperature of the flux reaches and exceeds the liquidus temperature of the electrode, and the electrode begins to melt. Metal droplets collect in a pool on the base plate and begin to solidify. As solidification proceeds, an ingot (secondary electrode forms with a molten pool of metal on top, beneath the rising bath of molten flux. The molten flux in contact with the water-cooled crucible solidifies during the melt to form a thin skin between the crucible and the solidifying ingot. This skin is responsible for the excellent ingot surfaces attained from electroslag melting. Near the end of the melt, the power can be reduced to eliminate the formation of pipe and centerline porosity.

In the late 1950's, reports were received from the Soviet Union concerning experiments in submerged arc welding of titanium using a flux. With this as a basis, the production of titanium ingots by the electroslag process evolved at the E. O. Paton Electric Welding Institute in Kiev. The Soviets were particularly interested in utilizing the electroslag process to obtain slab-shaped titanium ingots from which to roll sheet. Ingots with smooth, directly workable surfaces and better yield were obtained. Furthermore, expensive dc rectifiers were not required.

In the light of Soviet reports, personnel from the U.S. Army Materials and Mechanics Research Center, Watertown, MA, contacted the Bureau of Mines, and research on this subject was initiated at the Albany (OR) Research Center in 1965. The stated objective was to develop a process to produce slab-shaped titanium, with the understanding that the Soviet claims for the electroslag process would be evaluated.

Electroslag melting techniques have been successfully employed to produce high-quality ingots of superalloys and specialty-grade steels for several years. The electroslag process was believed to hold promise for melting reactive and refractory metals to give ingots with properties unattainable by consumable-electrode-arc melting or induction melting techniques. Zirconium was also thought to be a candidate for this melting technique since, to the authors' knowledge, no previous work concerning electroslag melting of this metal has been reported. Considerable interest was expressed by industrial representatives regarding the electroslag process as an alternative to conventional melting techniques for zirconium. Improvements in ingot chemistry to reduce or control impurities detrimental to ductility and mechanical properties were sought. In addition, electroslag melting produces smooth ingot surfaces that eliminate or reduce the need for expensive machining prior to working. A series of consumable-electrode zirconium electroslag melts was conducted under various operating conditions, and the products were evaluated with respect to impurities, resistance to corrosion, and mechanical properties to determine whether the aformentioned advantages of the electroslag process could be applied to zirconium.

SUMMARY

Melting techniques were investigated for purifying titanium sponge metal and consolidating sponge and scrap metal. Controlled-atmosphere electric arc melting, electric arc slag melting, and induction slag melting were successfully used. The titanium metal feed used in the arc melting techniques had to be fabricated into consumable electrodes. As in production of titanium metal by reduction processes, prevention of contamination by the atmosphere, adsorbed water, and refractory materials such as metal oxides and graphite was critical. Water-cooled copper crucibles were used to contain the molten metal.

CHAPTER 8.—ELECTROREFINING

In 1938, early in the Bureau's research on titanium, electrowinning appeared to be a desirable production method. However, it was realized that such an approach would necessitate much study, whereas the Kroll process appeared more promising for rapid development. Consequently, emphasis was placed on chemical reduction methods during the 1941-52 periods.

In 1952, when electrolysis was again examined, the choice of a suitable electrolyte was the first consideration. The literature contains reports by many investigators who tried to electrowin titanium from aqueous and organic solutions with little or no success. Work by the Bureau (*8*) substantiated that of earlier investigators.

Many active metals that are not amenable to aqueous electrolysis are successfully electrowon from molten-salt electrolytes. Aluminum, magnesium, and sodium are examples. Therefore, an investigation into the feasibility of using molten-salt electrolytes to electrowin titanium appeared to be warranted.

Electrowinning titanium from a molten salt presented many problems not encountered with most other metals. Its great affinity, when hot, for oxygen and nitrogen meant that all operations had to be performed in an inert atmosphere, and the high melting point of titanium precluded electrowinning molten titanium.

It was decided to concentrate, as a first step, on the development of an electrorefining process for recovering pure titanium from offgrade sponge, scrap, and alloys. In this way, such things as electrolyte composition, cell design, deposition conditions, and materials of construction could be investigated without having to contend with the problems involved in handling chlorine or other gases evolved at the anode. It was felt that the information obtained from developing the electrorefining process would assist in appraising the possibilities of electrowinning.

CHOICE AND PURIFICATION OF ELECTROLYTE

The electrolyte used in molten-salt electrolysis of any reactive metal must be stable and nonvolatile at the operating temperature, be an ionic conductor, dissolve the metal ions to be electrolyzed, and be inert to the container and the atmosphere (*9*). The ideal electrolyte should also have a low melting point, permit high current densities, and produce massive, coherent deposits. Because the deposits must be separated from occluded electrolyte by water leaching, it is desirable to use salts that can be recovered from solution in anhydrous form or that are cheap enough to be discarded. The same considerations apply to contaminated electrolytes.

The suitability of any electrolyte could only be determined by experimentation, as little had been published on similar work.

Since a low operation temperature appeared desirable, a eutectic mixture of MgCl-NaCl with a melting point of 450° C was examined. Electrorefining with $MgCl_2$-NaCl produced good metal having a Brinell hardness lower than 100 if the process was conducted at 750° C or above. However, 750° C approaches the melting point of single-salt electrolytes, such as NaCl, $MgCl_2$, and KCl. Electrorefining with a MgCl electrolyte showed that it was almost impossible to purify and maintain the $MgCl_2$ purity because of hydrolysis. KCl was serviceable, but expensive, and good metal was only obtained at low current densities. On the other hand, NaCl was inexpensive, easy to recover, easy to purify, and good metal was obtained at relatively high current densities. As a result of these considerations, NaCl was selected as the electrolyte. An operating temperature of 850° C was selected because the physical condition of the deposited metal was good, rate of metal deposition on the cathode was high, and the life of the equipment would be reasonable.

Purification in Bath

As the work progressed, it became apparent that the electrolyte must be purified before use. All commercial alkali metal chlorides, including NaCl, contain moisture in varying amounts. This moisture is not driven off entirely, even at the melting point of the salt, and hydrolysis takes place, forming oxides and oxychlorides that prevent the deposition of high-quality titanium. All of the molten-salt systems produced titanium of increasing purity on continued service until metal having a Brinell hardness varying between 65 and 85 could be recovered during the remaining life of the bath. This method of developing a serviceable electrolyte was attained at the expense of considerable life of the bath owing to the formation of sludge during purification.

In the search for a rapid, simple method of conditioning electrolytes, several different procedures were investigated, and as a result of these investigations, it became apparent that titanium would be deposited more efficiently from an electrolyte containing the titanium in a lower valent form, either $TiCl_2$ or $TiCl_3$. The formation of lower-valency titanium chlorides in the bath could be accomplished by reacting titanium metal with dry HCl gas or purified $TiCl_4$ beneath the surface of the molten electrolyte. While this method of conditioning the bath yielded satisfactory results, a more flexible way to achieve the same results was to prepare a "master" mixed salt containing a large quantity of $TiCl_2$, which was referred to as soluble titanium. Electrolytes containing any desired content of soluble titanium could then be prepared by mixing quantities of the master salt with fresh salt. The master salt was prepared by reacting sodium metal with $TiCl_4$ in a two-step reaction, as shown in the following:

$$4Na + TiCl_4 \rightarrow Ti + 4NaCl, \qquad (32)$$

$$Ti + TiCl_4 \rightarrow 2TiCl_2. \qquad (33)$$

Neglecting the formation of minor amounts of $TiCl_3$, and the presence of unreacted titanium metal, the product was essentially a binary mixture of $TiCl_2$ and NaCl.

Since melts consisting of titanium lower chlorides and NaCl can also be used as the starting material in a two-stage sodium reduction process to produce crystalline titanium metal, the Bureau carried out extensive research on methods to produce such melts.

Optimum Soluble-Titanium Content (*84, 119*)

A relationship, shown in figure 58, exists between the amount of $TiCl_2$ present in an electrolyte and the

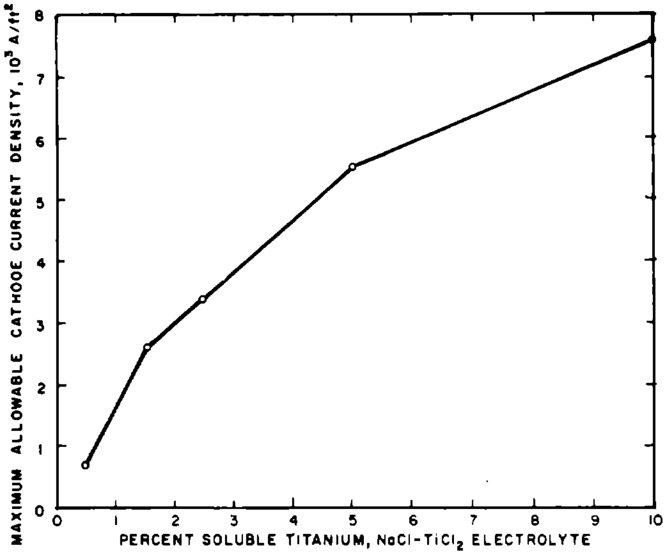

Figure 58.—Effect of soluble titanium content of electrolyte on maximum allowable cathode current density.

Table 40.—Effect of electrolysis time on electrolyte stability[1]

Test	Cell: Accumulative test time, h	Cell: Current efficiency, pct	Metal: Product, lb	Metal: Plus 34-mesh pct	Metal: Plus 34-mesh HB	Electrolyte: Soluble Ti, pct	Electrolyte: AEV	Electrolyte: Fe, pct
2 . .	12	59	17.4	79	74	5.0	2.09	0.02
4	24	60	17.8	69	72	4.9	2.08	.01
6 . . .	36	58	17.0	76	76	5.1	2.10	.01
8 . . .	48	60	17.6	74	79	5.0	2.12	.01
10 . .	60	58	17.2	70	78	5.2	2.10	.01

AEV Average effective valence.

[1] Cathode current density, 1,250 A/ft^2; average volts, 3.8; test time, 6 h; total current, 15,000 A·h.

Table 41.—Effects of $TiCl_2$ concentration on temperature limits for coarse metal product, degrees Celsius

Soluble Ti, pct	Max for coarse metal	Min for fluid bath	Min to max range for coarse metal
5.0.	870	830	40
8.5	840	790	50
10.5	830	770	60
13.2	820	740	80

NOTE.—Cathode current density, 500 A/ft^2.

maximum cathode current density that will produce high-purity metal. Allowable cathode current densities decrease rapidly as $TiCl_2$ content decreases below 5 pct. On the other hand, the greater loss of titanium caused by salt adhering to the deposits also makes concentrations higher than 5 pct less attractive. Furthermore, at the higher concentrations, disproportionation of $TiCl_2$ increases which results in increased $TiCl_3$ sublimation and increased losses of titanium.

In most of the Bureau's electrorefining work, including the operation of a 10,000-A demonstration cell, the $TiCl_2$ content of the electrolyte was, therefore, held between 4 and 5.5 pct. With 5 pct $TiCl_2$, cathode current densities up to 5,500 A/ft^2 would deposit crystalline metal with a hardness of <100 HB.

Electrolyte Stability (*122*)

In small-scale tests to determine electrolyte stability, 10 consecutive tests of 6 h duration were made at a current density of 1,250 A/ft^2. The data from alternate tests are shown in table 40. There was no increase in the hardness of the plus 34-mesh portion of the electrodeposit and the percentage of the plus 34-mesh produced was not changed appreciably.

The long life of the electrolyte under normal operating conditions with anode feed of moderate purity, was proven during 4 yr of cell operation. During this time, the electrolyte was discarded twice, and only because water leaked onto the hot metal surface, causing corrosion. The cell had a capacity of 450 lb of electrolyte and 250 lb of anode material.

Effect of Electrolyte Temperature on Deposits (*122*)

It was noted that when the electrolyte temperature was increased, a sudden change took place in the character of the deposit. Above a critical temperature, the crystals became very fine and the deposit was spongelike in appearance. To determine the critical temperature for electrolytes of different $TiCl_2$ content, a series of tests was made at 500 A/ft^2 cathode current density. The data shown in table 41 are the averages of five or more tests made at each concentration of $TiCl_2$. The data show that the critical temperature is lowered as the $TiCl_2$ concentrations increases. The data also show that the range of temperature over which acceptable metal is formed increases with increasing $TiCl_2$ concentration.

Dragout Ratio

Another factor that must be considered in determining current density and $TiCl_2$ content of the electrolyte is the loss of titanium incurred in the "dragout," which is salt entrained in the cathode deposit. With electrolytes of high $TiCl_2$ content, dragout can amount to as much as 1 lb of electrolyte per pound of metal. Usually, dragout is 0.5 lb of electrolyte per pound of metal. Reducing dragout improves the economy of electrorefining by reducing titanium losses. A lower dragout ratio results from the following conditions: deposits composed of coarse dendritic crystals, a sufficiently high temperature to assure a fluid bath, and avoidance of contaminants that increase the viscosity of the electrolyte. Dragout ratios as low as 0.1 lb per pound of metal were obtained in the Bureau's small-scale research. During 40 days of operation of the 10,000-A refining cell (*84*), dragout averaged 0.45 lb of electrolyte per pound of metal recovered.

CELL DESIGN

In molten-salt electrowinning or electrorefining of titanium, cell design and choice of construction materials are of primary importance. The cell must operate under an inert atmosphere and air must be excluded during operation. Construction materials must be capable of withstanding high operating temperatures for long periods of time and must not react with the molten-salt electrolyte. Several materials for cell construction were investigated. Some materials, such as metal oxides, could not be used because $TiCl_2$ reacted with them, which resulted in contamination of the electrolyte and the metal deposit. Iron, nickel, and molybdenum were found to be satisfactory. For manufacturing ease and economy, iron was used by many of the early researchers.

Early Cell Designs

The first cell used in the investigations is shown in figure 59. Mild steel was used throughout, except all external surfaces in the hot zone were plated with a chromium-aluminum alloy to reduce scaling.

The cell chamber, 1 in figure 59, was a 30-in length of standard 10-in-diam pipe. A 0.75-in steel bottom plate (2) was welded to one end, and a steel flange (3), provided with a water-cooling channel (4), was welded to the other end. The top (5), which was bolted to the flange (3), was water-cooled to protect the rubber gasket (6). Vacuum-tight rubber sleeves (7) and insulated caps (8) were the feedthroughs for the anode and the cathode. Provisions was made for evacuating the cell and filling with helium. Sight glasses (9) were installed to observe the progress of the experiment. During initial experiments, graphite crucibles (10) were used to contain the electrolyte. In the early work, considerable trouble was experienced with molten electrolyte leaking through the crucible. However, corrosion of the mild steel by the molten salt was negligible, and the use of graphite crucibles was discontinued. To facilitate removal of bath from the cells, thin steel crucibles were substituted for graphite.

This type of cell, while serviceable, was not entirely satisfactory because the cell had to be cooled to change electrodes or sample the bath. Heating and cooling the cell was time consuming and caused some of the $TiCl_2$ in solution in the electrolyte to disproportionate to titanium metal and volatile $TiCl_3$ resulting in loss of soluble titanium from the electrolyte.

The cell shown in figure 60 was designed with water-cooled receivers above the cathode and anode. Gate valves between the cell proper and the receivers prevented contamination of the cell by air during the changing of electrodes, and the receivers permitted metal deposits and bath samples to be cooled in an inert atmosphere before removal. The cell was used to investigate electrorefining with binary titanium alloys having nominal composition of 95 pct Ti and 5 pct of an alloying element (*147*).

A third type of cell, illustrated in figure 61, was used in special tests, such as alloy-purification experiments. This cell was operated in a manner similar to the cell illustrated in figure 60. It was essentially a double cell since it contained two nearly identical electrolyte baths, but had a common anode lead that divided and supported a perforated basket in each electrolyte. This cell was designed so that one electrolyte could be used as a control,

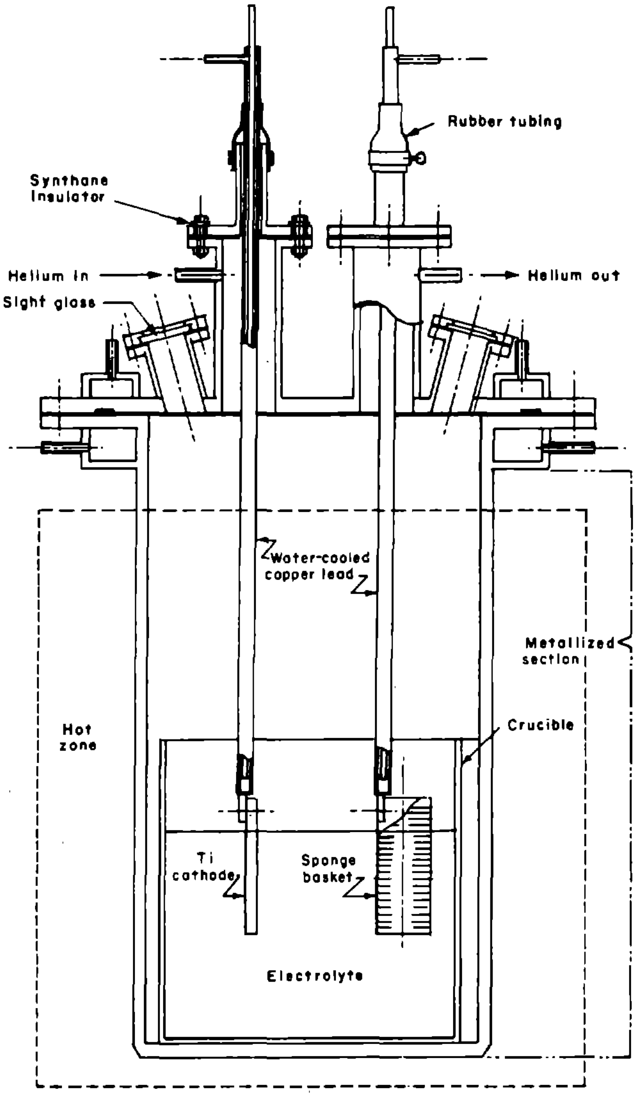

Figure 59.—Cross section of cell used in earliest investigations.

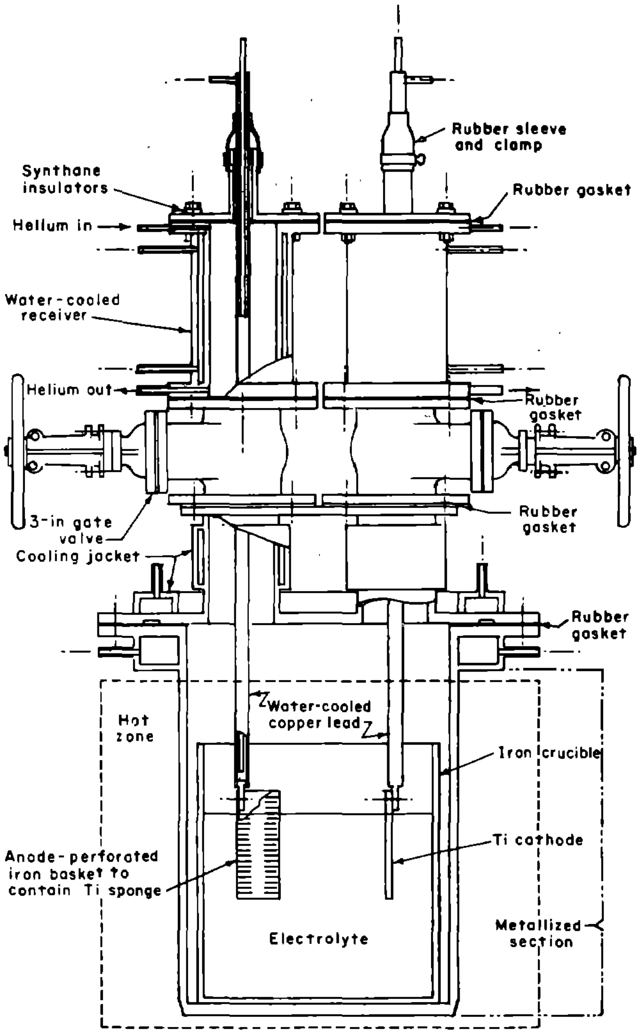

Figure 60.—Cross section of first continuous operation cell.

using materials with known electrorefining characteristics in the anode basket, while the other was used to examine the electrolyte being tested. As long as the control cell produced good metal, any variations in the metal produced in the other cell were assumed to be due to the electrolyte. This cell has the disadvantage that, although cathodes could be changed at will, the anodes could only be changed when the cell was cold.

The three cells described were adequate for research where quantity of deposit was not a primary consideration. The size of the cathode deposits in these cells was limited by the inside diameter of the valves through which the deposits were withdrawn. In most instances, less than 150 g was deposited.

Because of a growing need for very pure titanium in other investigations, a cell that could produce deposits up to 800 g was designed and operated. This cell, known as the B cell, is illustrated in figure 62. It was rectangular and consisted of three main sections: the lower section containing the molten electrolyte, a cooling chamber, having water-cooled walls, and a change box. The lower section contained a rectangular crucible made from 3⁄16-in mild steel. Two perforated sheets of 1⁄8-in steel were welded on diagonally opposite corners of the crucible to form two triangular anode compartments into which offgrade sponge could be placed as required. The cooling chamber was separated from the bottom section by two water-cooled half lids, each having an opening for a water-cooled electrode lead, thus permitting the doors to be closed during electrolysis. This feature was necessary to confine the sublimate and also to reflect heat to the lower section of the cell. The doors also kept the upper chamber cool enough to permit the cell operator to work with his or her hands inside the cell. These doors could be rotated upward through 90° and were opened when deposits were removed, new cathodes lowered, titanium sponge added to the anode compartments, or makeup salt added to the electrolyte. Changing of cathodes, making additions, and sampling were accomplished by working inside the cooling chamber through rubber gloves installed on two adjacent sides. The helium system was designed so that the cell and change box could be purged independently or together.

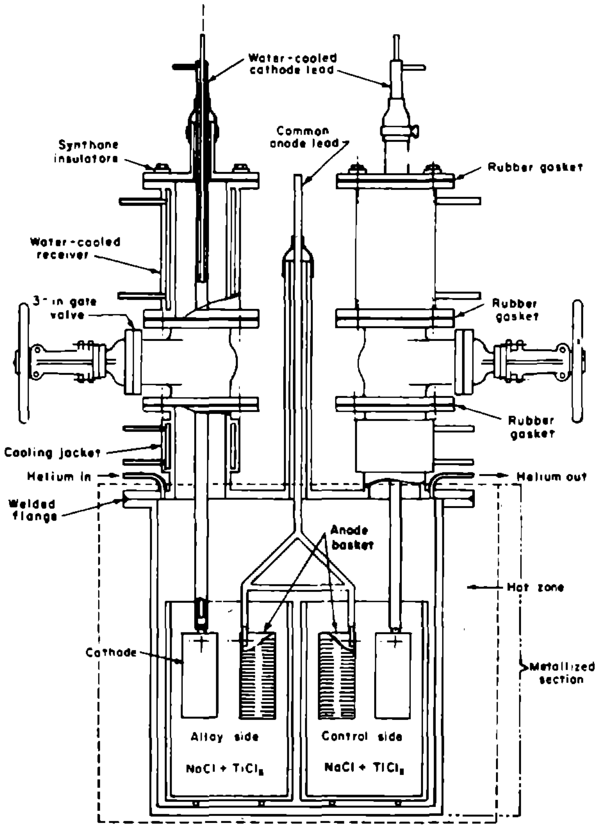

Figure 61.—Cross section of dual electrolyte cell.

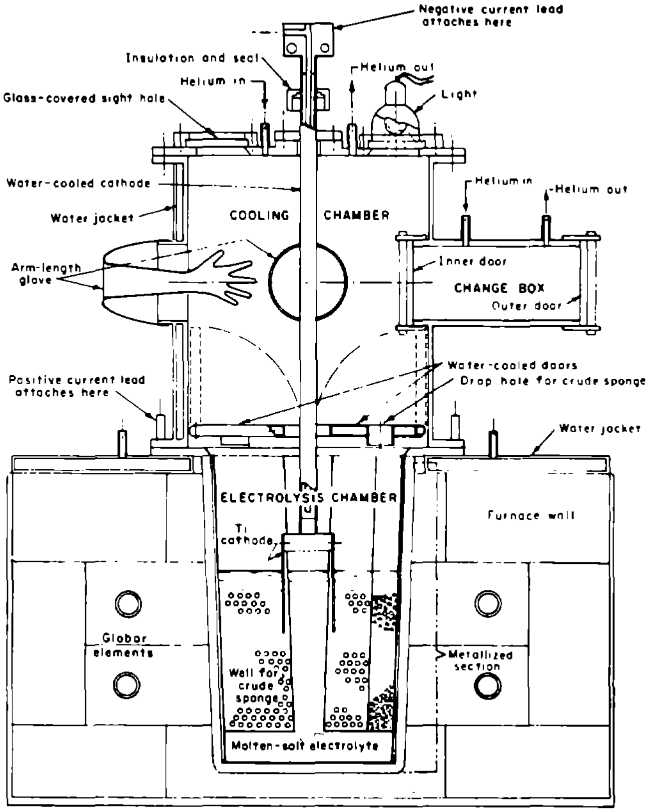

Figure 62.—Cross Section of B cell.

Deep-Bath Cell (*10*)

In an effort to obtain greater capacity by increasing the depth of cathode immersion for deposition, a cell was designed to hold an electrolyte bath up to 41 in deep, permitting cathode immersions up to 30 in. The cell, shown in figure 63, was 27 in. in diam and 60 in deep and could hold up to 1,400 lb of electrolyte. The scrap titanium used as the anode in these experiments was placed in the bottom of the cell.

In a series of 20 production-type cycles, the cell produced 11.5 lb of metal per cycle at an average cathode current efficiency of 72.0 pct. The metal had a Brinell hardness ranging from 65 to 79.

Internally Heated Cell (*123*)

The cells used in early electrorefining studies were heated externally by SiC resistance elements. The possibility of internal heating was suggested by the fact that the inside surfaces of the electrolytic cells, both above and below the bath, remained in good condition after long use. Thus it seemed reasonable that an internal heater would resist corrosion under these conditions and would be a practical means of heating the cell. Also, iron and stainless steel cathodes in the cells lasted approximately 6 months under continued operation, even though the temperature of the cathodes was higher than that of the bath when high rates of deposition were used.

Advantages of an internally heated cell included higher energy efficiency and a simpler structure. Also, internal heating would facilitate surrounding the cell with an inert atmosphere that would extend its life.

Important questions were whether the high surface temperature of the heating element would cause deterioration of the bath and whether ac heating current would interfere with electrolysis.

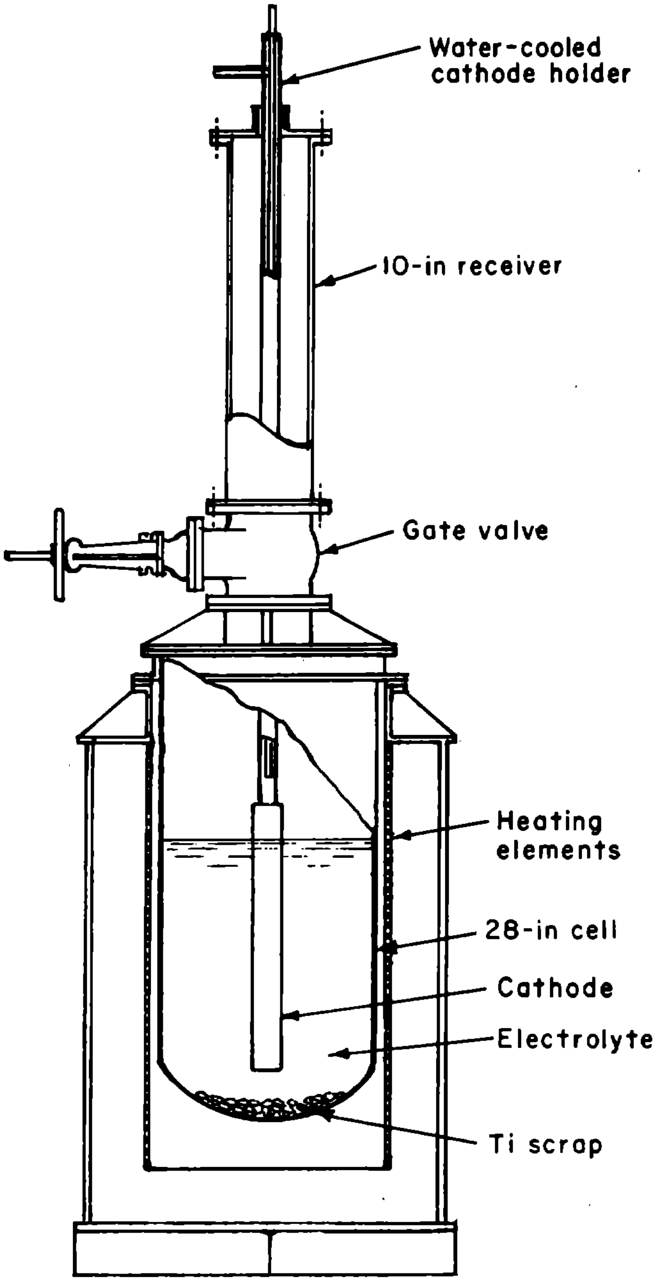

Figure 63.—Cutaway of deep-bath electrorefining cell.

Preliminary studies were made in a laboratory cell that employed two 7/16-in-diam mild-steel rods for internal heating elements. The cell, shown in figure 64, was fabricated from mild steel. The bottom was a 30 in length of standard 12-in pipe, with a plate welded to the bottom end to form the bottom, and a water-cooled flange welded to the top end. The cell cover, bolted to the flange, was also water-cooled to protect a rubber gasket seal. A 4-in opening in the center of the cover was formed by an elevated flange, to which was bolted a water-cooled, rubber-gasketed, 4-in slide valve, with a water-cooled receiver attached. The cathode was a 3/4-in stainless-steel rod 8 in long. Packing glands formed a seal where the heating elements entered the cell. Silicon carbide resistance bars in the containing furnace supplied external heat to maintain the operating temperature of 850° C.

Only five cycles were completed with this cell. Inadequacy of the heating elements to keep the bath molten, overheating of the leads, scorching of the synthane insulators, and fusion of the feed material around the elements brought about the early termination of tests.

Results with the first cell were sufficiently encouraging to warrant additional investigation of internal heating, and another cell was designed and constructed.

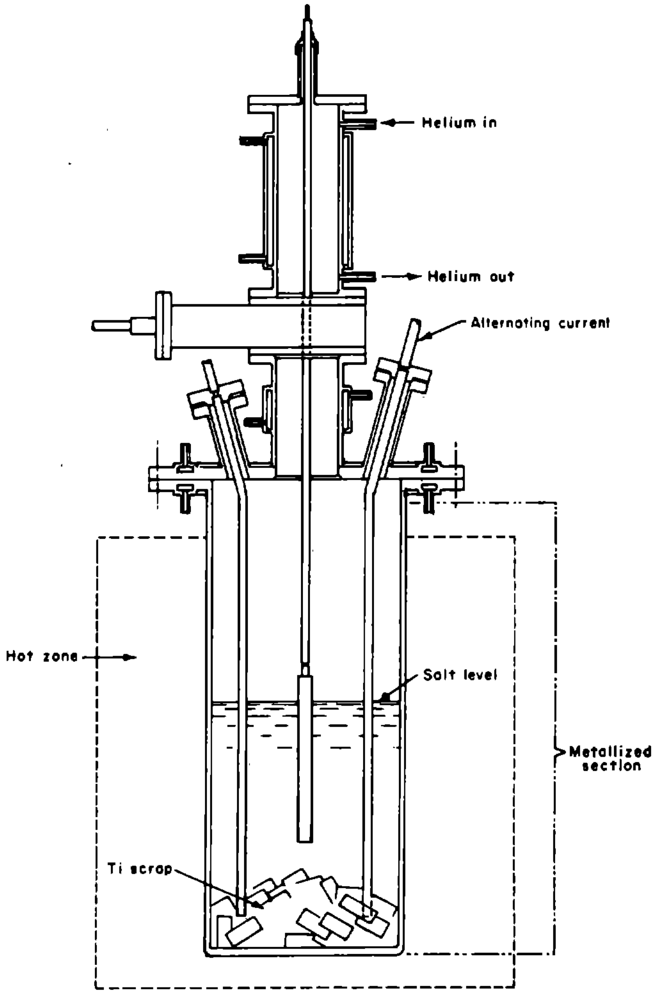

Figure 64.—Diagram of internally heated laboratory cell.

Figure 65 shows the end view of two cross sections of this cell. Section A is a half cross section of the two end ports and shows the port accommodating the dc electrode assembly and receiver unit. Section B is a half cross section of the two center ports accommodating the ac heating unit.

Ports to accommodate the cathode and internal heater assemblies were placed in two parallel rows with three ports in each row. The cell bottom was 20 in deep, 21.5 in wide, and 34.5 in long. A 3-in-wide flange was welded around the outside edge of the pot rim, and the outer edge of the flange was, in turn, welded to the bottom edge of the top structure to form a sealed unit. This flange carried some of the loaded cell weight by resting on a layer of hard firebrick. Backing the firebrick was 9 in of insulating brick for the cell sides and 18 in for the bottom. An outer steel case completed the enclosure.

The lower supporting frame of the top structure was built of three half sections of standard 12-in steel pipe placed side by side. The two paired edges were welded together to form a unit of three arches that were closed by welding two plates to the open ends. Two 5-in lengths of standard 8-in steel pipe were welded to two equispaced port openings cut through the tops of all three arches to form six ports. These were flanged at the top for attachment of slide-valve assemblies and receivers and were fitted with water jackets for cooling.

The two water-cooled, 1.75-in, mild-steel ac electrodes entered the cell through the two center ports. Packing glands that could be loosened to permit depth adjustment formed a seal around the electrodes. The ends of the 5.5-in-diam melt-starting coil were welded to the electrode ends. This 12 in length of coil was formed from an 81 in length of 0.5-in mild-steel rod. This coil served as a resistance heater to initiate melting of the surrounding salt. When the heat from the coil had melted enough salt to form a pool between the electrodes, the current then flowed through the more conductive molten salt.

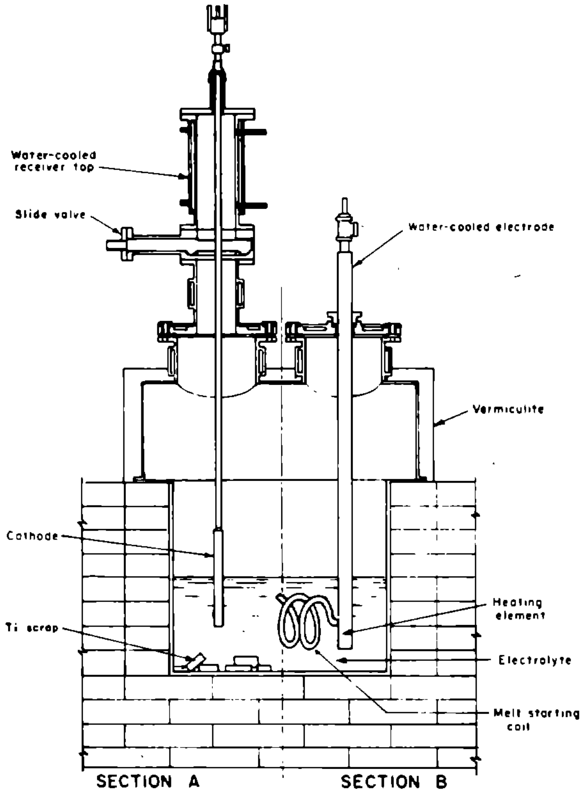

Figure 65.—Diagram of internally heated cell.

Development of 10,000-A Cell (*84*)

An investigation by the Bureau of the commercial possibilities of electrorefining titanium was sponsored by the General Services Administration. A 3-yr program starting October 1, 1957, covered the design, fabrication, and installation of a 10,000-A cell with power sources and necessary auxiliary equipment. Operation variables were investigated, material handling procedures were developed, and the cost of refining titanium scrap was determined. The object of the program was to obtain data for evaluating the process for the production of high-purity titanium from poor-quality Kroll sponge or industrial scrap.

The prototype cell design was based on several empirical relationships established in the smaller scale investigations:

1. The electrolytic current should not exceed 4 A/lb of electrolyte.
2. The initial cathode current density should not be greater than 1,000 A/ft^2.
3. The maximum weight of the deposit should be limited to 0.1 lb/in^2 of cathode surface area.
4. The anode surface area should be at least twice that of the cathode.

Electrolyte Chamber

Small-scale tests showed that low-carbon steel was a suitable material for constructing the cell and electrodes. However, at the operating temperature of 850° C, its creep strength is very low, and stresses in the cell must be minimized. Local overheating must also be avoided, since titanium reacts with iron at 1,050° C to form a eutectic alloy. Extreme care is necessary in welding cell components because the molten electrolyte (NaCl-$TiCl_2$) penetrated the smallest pinhole.

Figure 66 shows a cross section through the longitudinal axis of the 10,000-A cell. The electrolyte chamber had

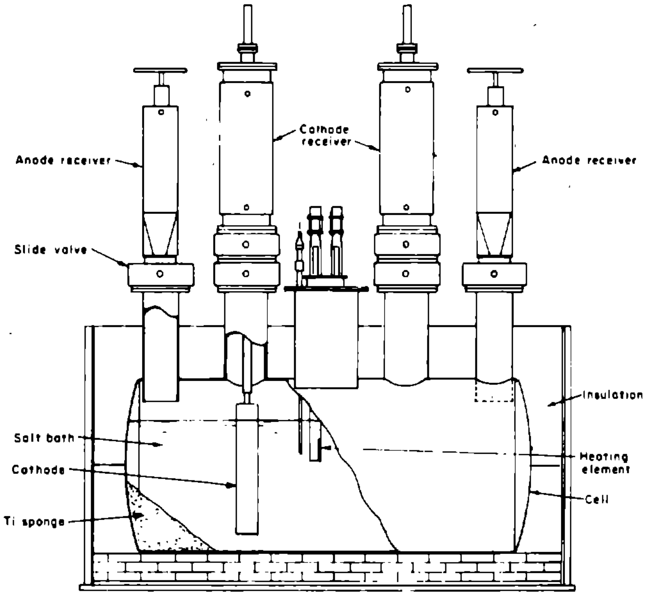

Figure 66.—Cross section through longitudinal axis of cell.

an inside diameter of 4 ft and an overall length of 9 ft 8⅝ in. It was fabricated from A-285, grade C flange-quality steel with type 310 stainless steel cladding on all external surfaces. Wall thickness was ⅝ in except for the nozzles, which were fabricated from 0.5-in clad plate.

Use of a cylindrical form with nozzles for cathode and anode openings gave maximum hoop strength, distributed the weight of the superstructure over a wide area, and allowed those parts of the cell that operated at elevated temperatures to be covered with a minimum of 9 in of insulation. Carbon steel is not normally used at temperatures in excess of 540° C. Its short time proportional limit approaches zero at 650° C. At higher temperatures, carbon steel will creep with little applied stress. To prevent deformation, it was necessary to use castable insulating cement to support the lower half of the electrolyte chamber. Weight of the superstructure was carried on cross braces. With this arrangement, the cell maintained its shape at 850° C.

Defective welds led to early failure with the first electrolyte chamber. Minute perforations extending through the inner steel wall led to catastrophic attack of the type 310 stainless steel cladding. Although mild steel will not react with the $NaCl-TiCl_2$ electrolyte in a helium atmosphere, stainless steel is rapidly corroded at 850° C in the presence of air. A spare electrolyte chamber was placed in operation on August 13, 1959, and was still in excellent condition when the operation was terminated on March 28, 1960. Service time was too short to permit an accurate estimation of pot life. However, some laboratory cells were used for over 3 yr with no sign of deterioration.

Superstructure

The superstructure for the prototype cell consisted of cathode receivers, anode receivers, and slide valves arranged as shown in figure 66. A cross section of the cell through a cathode receiver is shown in figure 67. Cathodes were made from 36-in lengths of 6-in-OD by 0.5-in wall seamless steel tubing. These were bolted to the bottom of 9-ft lengths of 1.5-in double extra-heavy hard-drawn copper tubing that were internally water cooled.

Cathode receivers were made from 3.75-ft lengths of 1-ft-OD schedule 40 steel pipe and were fitted with external water jackets. Cover plates for the receivers were insulated from the cell with plastic bushings. A rubber seal at the center of the cover plates kept air from entering the cell when the electrodes were raised or lowered. Similar seals were used on all other moving parts. Flat gaskets between bolted sections were made of fluorinated synthetic rubber (Viton) to avoid water cooling.

Before the cell was placed in operation, the cathodes were positioned in the receivers and both the top and bottom slide valves shown in figure 66 were closed. The top valve contained a single, rectangular water-cooled slide, 14⅝ in wide by 15 in long by 1¼ in thick. When it was in place under the receiver, the rubber-gasketed top surface of this slide could be raised against a circular seat to form a vacuum-tight seal. This type of valve, which was developed at the Bureau's Boulder City (NV) Research Laboratory, was successfully used in a number of electrorefining and electrowinning cells. The lower valve shown in figure 66 contained two water-cooled slides. One, 14⅝ in wide by 7¾ in long, was used only during deposition. It was operated from the rear of the cell. The front slide was the same as that used in the upper valve except for a 1-in-radius half circle cut into its leading edge. A matching half circle was located in the back slide. Both half circles were lined with insulating cement to prevent short-circuiting between the electrodes and the slides.

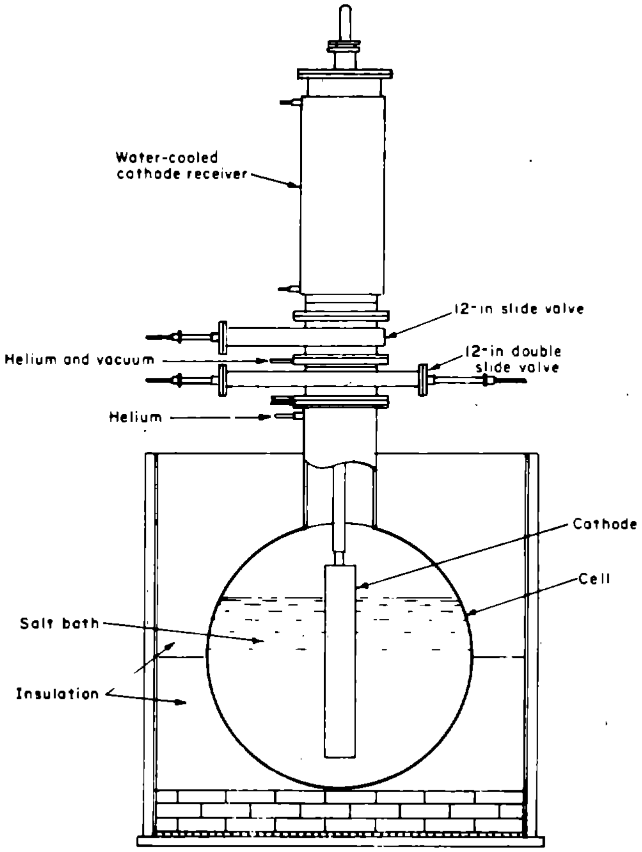

Figure 67.—Cross section of cell at cathode receiver.

To start a run, cams on the top valve were unlocked and the slide was pulled out while the bottom valve remained closed. The receiver section was then evacuated and filled with helium three times. The bottom slide valve was then opened and the cathode was lowered into the electrolyte, usually to an immersion depth of 30 in. The two slides of the bottom valve were butted together in the center of the receiver opening before electrolysis was started. The half circles in their leading edges joined to form a 2-in opening surrounding the cathode lead. This confined sublimate to the lower section of the cell and prevented condensation of vapors on the inner water-cooled surfaces of the receivers.

When deposition was complete, the cathodes were raised above the electrolyte and the deposits were allowed to drain for 15 min to remove as much salt as possible. The two slides on the lower valve were then pulled out, and the deposit-laden cathodes were raised into the receivers to cool. The front slides of both valves were then pushed in and the cams were turned, sealing off both the receivers and the cell. Subsequently, the receivers were unbolted between the top and bottom slide valves and the deposits were allowed to cool to room temperature. Spare receivers, complete with slide valves and cathodes, were bolted on the cell, and the cycle was repeated.

Figure 68 shows a cross section of the cell through one of the anode receivers. The receivers for the prototype cell were large enough to contain a full week's supply of anode

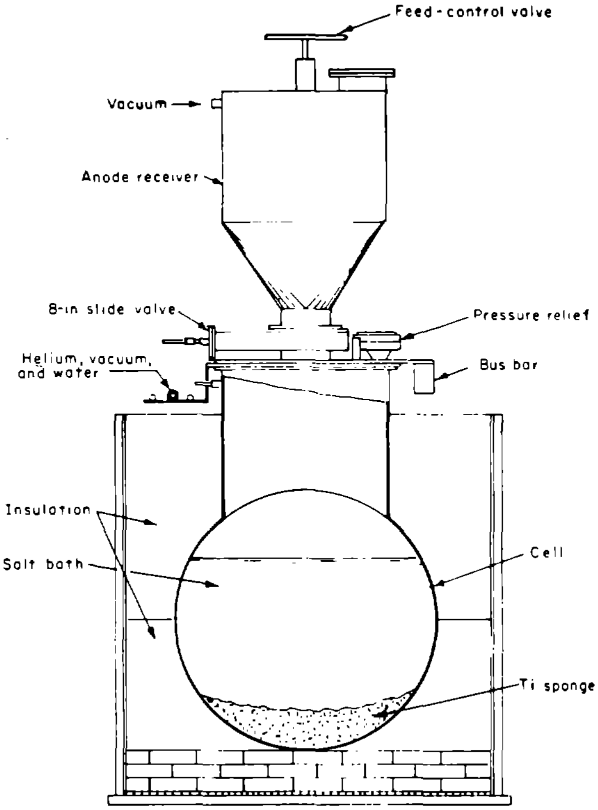

Figure 68.—Cross section of cell at anode receiver.

material. Titanium sponge or scrap was added to the receivers through the openings at the top with the lower slide valves closed. After the cover plates were replaced, the anode receivers were evacuated and filled with helium three times and the slide valves were opened. Anode material could then be dropped into the electrolyte at will by raising handles at the top of the receivers, which lifted a steel plug at the bottom of each receiver.

As titanium was transferred to the cathodes, a fine sludge containing most of the impurities was left behind. The sludge blanketed the remaining anode material, reducing its effective area. It also prevented good electrical contact between subsequent additions of anode material and the sides of the electrolyte chamber. In extreme cases, sludge rendered the cell inoperative. In most cases, however, sludge caused a gradual rise in the cell resistance and caused smaller crystals to form on the cathode. To bring conditions back to normal, it was necessary to stir up the material at the bottom of the cell with a poke rod. The prototype cell was not equipped with poke rods and it was, therefore, necessary to remove the anode receivers periodically and replace them with a special receiver fitted with a long steel rod having a spade tip. Changing receivers was time consuming and it was recommended that any future cell be equipped with a permanent poke rod arrangement.

Internal Heater

Laboratory cells were externally heated using either SiC rods or metallic resistance elements. Heating in this manner, although acceptable on a small scale, was expensive, since heat losses were difficult to control or eliminate. To overcome this drawback, an internal heater, shown in figure 69, was devised for use in the prototype cell. Design of this heating system was similar to that described earlier in this chapter except that there were four main heating electrodes instead of two, and these consisted of 5-ft lengths of 3-in square steel bar.

When the cell was put into operation for the first time, the electrolyte chamber was filled with granular NaCl. The internal heating assembly was then bolted in place in the 18- by 24-in center opening of the cell with the bottom of the electrodes immersed in the salt. Alternating current was passed through the starting coil to melt the salt in the vicinity of the main electrodes. Heat for melting the remainder of the salt and holding the electrolyte at operating temperature was supplied by passing current through the bath between the two sets of main electrodes. The starting coil was disconnected and raised out of the bath as soon as curent could be passed between the main electrodes.

The voltage across the electrodes could be controlled by raising or lowering the electrodes. Convection usually proved sufficient to keep the electrolyte well mixed. Operation of the internal heater was satisfactory throughout the test period.

Electrical Components

The 150-kVA rectifier had a maximum dc rating of 10,000 A and a control range of 1.5 to 15 V. Power for the internal heater was supplied by a 100-kVA transformer having a maximum rating of 4,000 A at 25 V and a control range of 5 to 25 V. Controls were provided for stepless, remote operation for both the rectifier and the transformer.

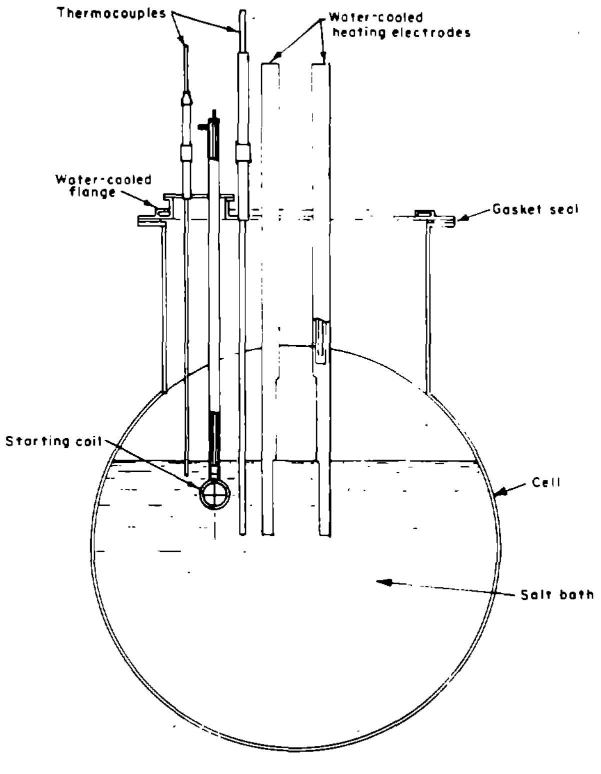

Figure 69.—Cross section of cell through internal heater.

Other Titanium-Refining Cells (*119*)

Three electrorefining cells were designed to investigate the electrorefining of reject-grade titanium sponge. Operation of the cells provided information on the effects cell design and operating variables had on the quality of the product. The electrolyte chambers had capacities ranging from 400 to 3,500 lb of molten salt. Major factors investigated were electrolyte composition, temperature and cell life, cathode shapes, materials of construction, methods for removing cathode deposits, current density and cell potential, and the mechanics of deposit growth and crystal morphology.

One of the cells was in intermittent operation over a 4-yr period and produced 2 st of refined titanium. A product with a hardness of 80 HB or less was consistently obtained. Some metal with a hardness of less than 60 HB was produced. In one of the cells in which the electrolyte was held at operating temperature with an internal heater, an ac input of 25 kVA maintained 3,500 lb of electrolyte at 850° C, but with an external heater, 35-kVA input was required to maintain 400 lb at 850° C.

A cutaway view of cell 1 is shown in figure 70. Mild steel was used for the cell structure. The cell had a capacity of approximately 450 lb of electrolyte and 250 lb of anode material. The three openings in the top section were 6.5 by 12.5 in. Each entry compartment included a cover, receiver, and double slide-valve assembly as previously described.

Figure 71 shows a cutaway view of cell 2. The chamber was the same size and capacity as cell 1; however, a perforated screen with ⅛-in-diam holes confined the feed material within the center compartment and allowed ion migration and circulation of electrolyte. This freed the outer compartments of anode material. Besides containing the anode material, the center compartment served as receptacle for replacement of salt and addition of anode metal. These materials could be added at any time, even during electrolysis. A rod inserted through the cover entrance of the center compartment was used to poke the anode material to free it of residue and maintain better electrical contact. The rod was also used to scrap the screen surface to prevent blockage of the perforations.

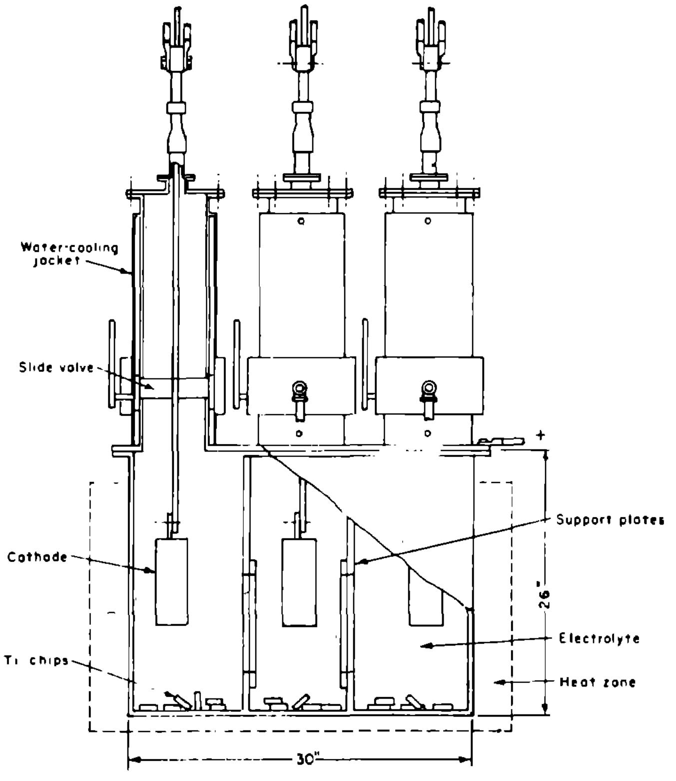

Figure 70.—Cutaway view of cell 1.

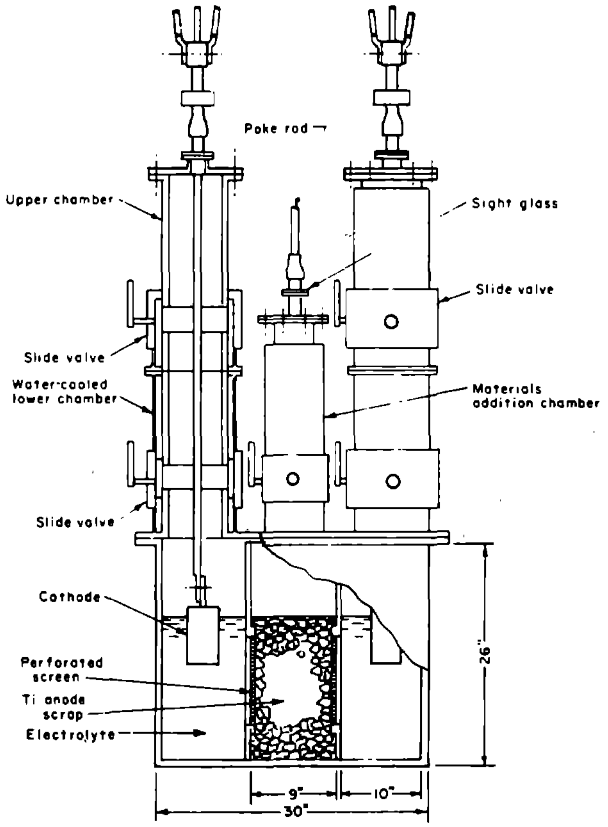

Figure 71.—Cutaway view of cell 2.

Cell 3 was constructed to combine the advantages of the deep-bath cell (*10*) and the internally heated cell (*123*) previously described. A perspective view of this cell is shown in figure 72. The elliptically shaped, flat-ended chamber was constructed of ⅜-in mild-steel plate and was 60 in long, 46 in deep, and 24 in wide. The two internal heating electrodes, shown in the cross section of the cell in figure 73, were made from 2-in square bars of mild steel. Electrodes were shaped with double bends to reduce their 12-in spacing at the cover to 3 in at the electrode level. This 3-in spacing facilitated the forming of an electric arc when melting of the salt was initiated. The arc was struck at the desired depth by manipulating a piece of graphite between the electrodes. Five minutes of arcing formed a molten pool between the electrodes and thereafter, melting progressed rapidly.

The 3.5- by 5- by 7.5-ft shell that contained insulation surrounded the chamber and provided a minimum of 8.5 in of insulation. Approximately 3,500 lb of salt and 400 lb of anode material were used, which resulted in a 34-in bath depth.

The cell shown in figure 74 used a 12-in-diam electrolyte chamber lined with a graphite crucible and was provided with slide valves to isolate the electrolyte

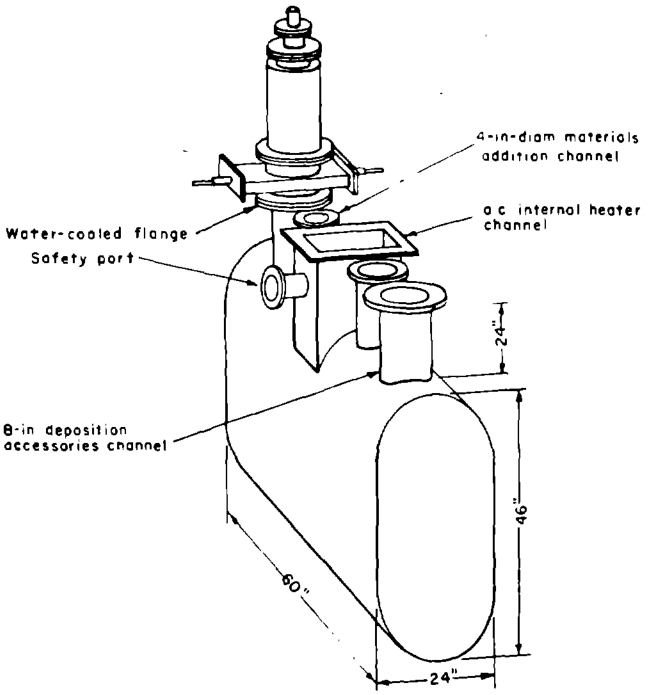

Figure 72.—Perspective view of internally heated cell 3.

chamber from the receivers. This type of cell was used in investigation of a two-stage electrolytic processes (*220*). In this process, crude titanium metal was made by electrorefining a compound, such as TiC, and then high-purity metal was produced by electrorefining again. This cell was also used in studies on electrorefining titanium ternary alloys.

Figure 75 shows a cell used in studies to determine the transfer rates of alloying constituents from molten titanium anodes to solid titanium cathodes in molten salt systems (*110*). The cell consisted of an electrolyte chamber and a receiver assembly, bolted together and sealed by a neoprene gasket. The 4-in-diam electrolyte chamber was fabricated from type 310 stainless steel and was lined with a graphite crucible. The molten alloy on the bottom of the crucible was anodic during electrolysis. The receiver assembly was composed of a flanged adapter, a water-cooled slide valve, and a water-cooled receiving chamber. The cathode lead was a 0.5-in mild-steel rod equipped with detachable titanium or mild steel cathodes.

OPERATING PROCEDURES

The following operating procedure, which applied to the deep bath cell (*10*), is typical of the procedures followed in most of the Bureau's electrorefining investigations:

1. The cathode was bolted to the water-cooled copper-cathode lead and sealed in the cell receiver.
2. An inert atmosphere of helium was established within the receiver chamber by purging the receiver for 2 h.
3. The valve that sealed the receiver from the cell was opened and the cathode lowered until contact was made with the bath, as indicated by an ohmmeter.
4. The cathode was immersed to a predetermined depth.

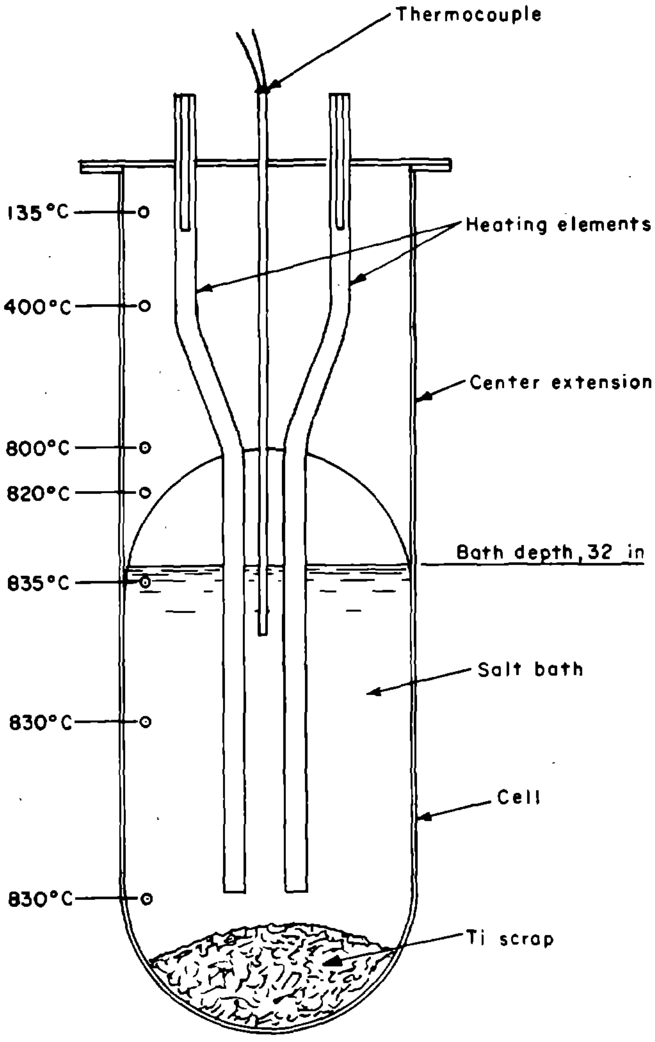

Figure 73.—Cross section of cell 3 through internal heater and temperature gradient.

5. A predetermined quantity of direct current power was applied for a specific time to produce a deposit.
6. The cathode was withdrawn from the electrolyte until the electrical circuit was interrupted, leaving the cathode and deposit positioned just above the bath, where it drained for 15 min.
7. The cathode and deposit were raised into the receiver chamber, the valve was closed, and the deposit was allowed to cool 1.5 h to room temperature.
8. The receiver was opened and the deposit was recovered by mechanical stripping.
9. The cathode was returned to the receiving chamber to repeat the cycle.

The stripped deposit, which consisted of titanium metal and occluded electrolyte, was weighed, leached with a mechanically agitated solution of 5 pct by volume HCl in water in a glass-lined, water-cooled tank, washed with water until free of salt, dried, and sized by screening into plus 8-, minus 8-plus 34-, minus 34-plus 48-, minus 48-plus 120-, and minus 120-mesh fractions. Samples of these sized fractions were evaluated by chemical analysis, and hardness was determined on an arc melted button.

Details of operation of the 10,000-A demonstration cell have been discussed earlier in the section of this

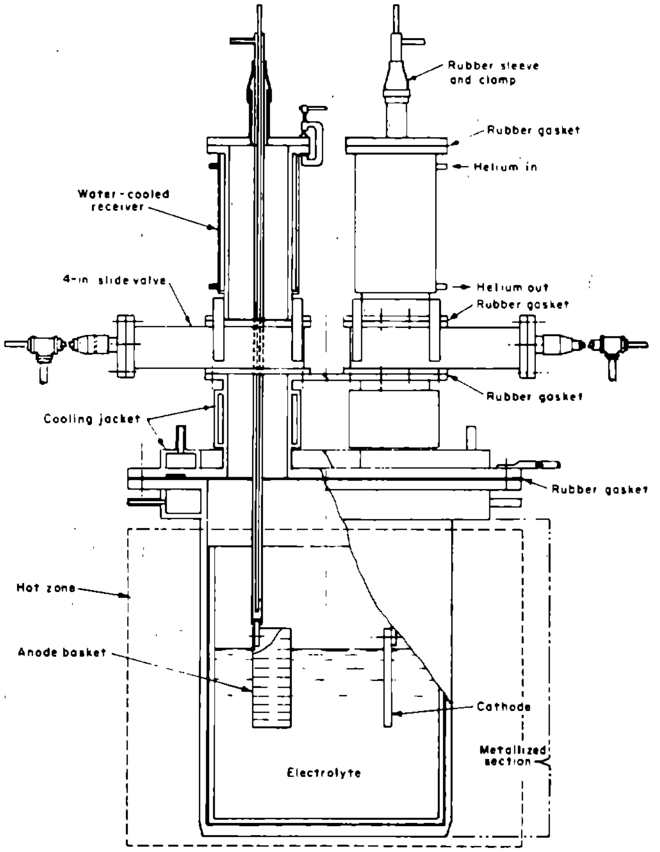

Figure 74.—Diagram of cell used in electrorefining tests.

chapter describing the design of the superstructure of that cell. Figure 76 shows a flowsheet developed for production of high-purity titanium from scrap or offgrade sponge based on the investigations conducted in the 10,000-A cell.

RESULTS OF INVESTIGATIONS

Early Experiments

Initial electrorefining studies (*145*) established that offgrade sponge and scrap, which contained oxygen, nitrogen, and iron as impurities, could be electrorefined to produce metal in which the plus 34-mesh fraction was softer than 80 HB. Titanium was also refined from certain elements found in commercial alloys (*85*). Molybdenum and chromium were successfully eliminated but manganese was not.

The cathode current density that was obtained at a given voltage depended largely on the concentration of soluble titanium chloride in the electrolyte.

Analysis of the electrolyte showed that virtually all of the titanium in the electrolyte was in the divalent state. The analytical procedure involved oxidizing titanium with chromic acid. The excess chromic acid was then titrated with a standard ferrous iron solution, which yielded the average valence of the titanium in the electrolyte.

Electrorefining of Titanium From Alloys (*146-147*)

Tle electrodeposition of titanium from seven binary alloys of titanium was investigated (*147*). The object of these experiments was to determine the efficiency of titanium separation from alloying elements under established conditions. The alloys tested were prepared from electrorefined titanium and 5 pct by weight of manganese, vanadium, aluminum, chromium, tin, zirconium, or molybdenum. Two methods were used in the investigation. In test method 1, the alloy anode was removed between tests, cleaned to present a fresh surface, then returned to the cell for the next test. In test method 2, the alloy anode was not cleaned between tests but remained in the cell.

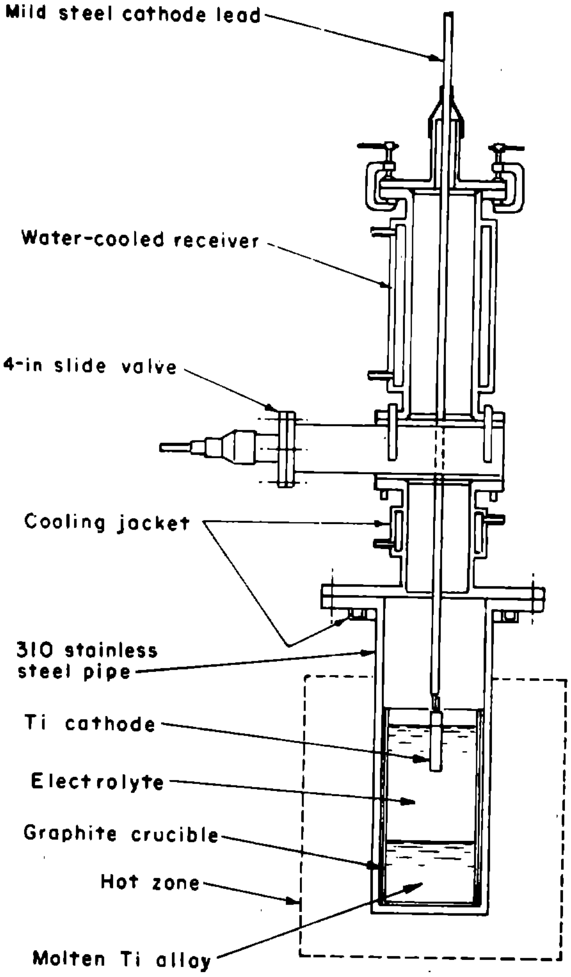

Figure 75.—Electrolytic cell.

Under the operating conditions of the experiments, the relative quantity of the alloying elements transferred fell into three distinct groups. In the first group were tin, zirconium, and molybdenum—elements with very low transfer. Aluminum and chromium, which comprised the second group, transferred only slightly in test method 1 but transferred more in test method 2. The third group, vanadium and manganese, transferred readily regardless of the test method used.

In another investigation (*146*), ternary alloys containing 2.5 pct of each of 10 metal pairs selected from the same elements used in the binary study were electrorefined. The transfer characteristics of the added metals in the ternary alloys followed the same pattern as the binary alloys. Manganese transferred most readily, followed by vanadium and chromium. Transfer of other metals never

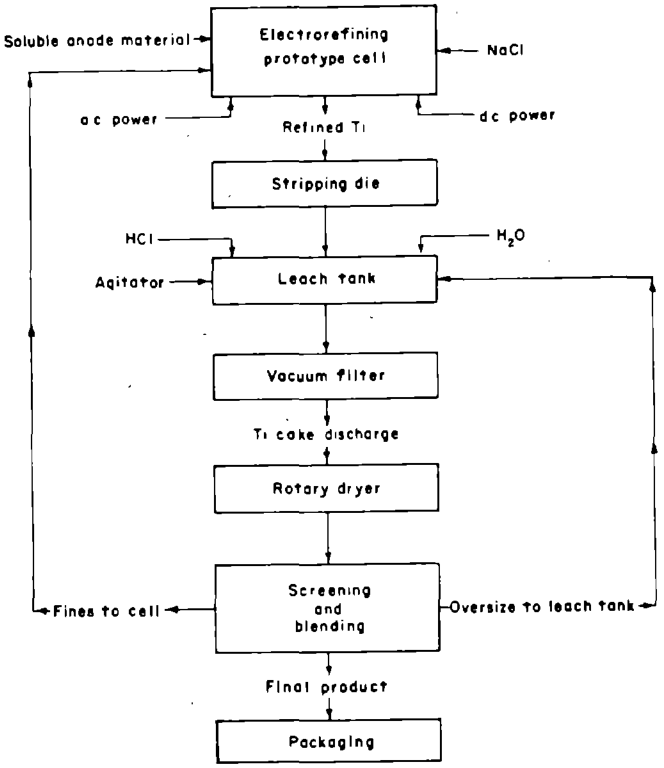

Figure 76.—Flowsheet developed for production of high-purity titanium from scrap.

exceeded 0.10 pct. Molybdenum depressed the transfer of the other minor metal in the three tertiary alloys that contained it.

Electrolytic studies were also conducted (*110*) to determine the transfer rates of alloying constituents from molten titanium anodes to solid titanium cathodes in molten-salt systems.

The metals nickel, tin, copper, bismuth, and manganese were selected on the basis of thermodynamic data and the melting point of the alloy systems. The transfer of nickel, tin, and bismuth was very slow. The cathode contained less than 0.01 to 0.001 pct of these elements. Copper transfer was 0.6 to 0.8 pct in electrolytes containing titanium chlorides and 0.12 pct in fluoride systems. Manganese transferred at a rate comparable to that of titanium. High-purity titanium and titanium-manganese alloys of uniform composition were produced by electrorefining molten titanium alloys in chloride electrolytes.

Electrolytic Methods of Preparing Cell Feed (*220*)

After electrorefining of offgrade sponge was developed by the Bureau, attempts were made to develop a two-stage electrolytic process for production of high-purity metals. In this process, crude titanium metal was made by electrorefining an inexpensive (or potentially inexpensive) titanium compound, and then high-purity metal was produced by electrorefining the intermediate product.

Electrorefining of TiC or a material consisting of titanium, carbon, nitrogen, and oxygen, and known commercially as titanium cyanonitride, in all-chloride electrolytes, yielded only a low recovery of titanium. Recoveries of titanium were much improved in a $NaCl-K_2TiF_6$ electrolyte—as high as 91 pct for TiC and 62 pct for titanium cyanonitride. The $NaCl-K_2TiF_6$ electrolyte was the most promising of all electrolytes tested because titanium recovery was high and the electrolyte was stable at the operating temperature.

The extent of titanium recovery from TiC was largely dependent on the surface of the anode material. Increasing the surface area increased recovery. However, titanium carbide in powder form dispersed in the bath and contaminated the product.

The titanium cyanonitride disintegrated to finely divided particles during electrolysis. Again, the residues disbursed in the bath and contaminated the product. The recovered titanium was mainly from that which was present as nitride and carbide. Most of the titanium that was associated with the oxygen appeared not to be easily recovered as a desirable product.

Metal produced from either feed was of fine particle size, and as a result, a large amount of electrolyte was entrapped with the deposit. Also, because of the fine particle size, the metal had to be consolidated before it could be used as cell feed for electrorefining. Furthermore, the product contained a high concentration of impurities. Selected metal products from electrolysis of TiC and titanium cyanonitride were cursorily tested as anode feeds in electrorefining with a $NaCl-TiCl_2$ electrolyte. The crude metal produced from TiC gave better results (73 to 78 HB) than that produced from cyanonitride (83 to 95 HB).

Electrorefining Titanium-Oxygen and Titanium-Nitrogen Alloys

The effect of oxygen in anode material on titanium electrorefining was studied (*124*). Increasing the oxygen concentration of the anode resulted in increased anode scale, decreased anode and cathode current efficiencies, lower titanium recoveries, and higher oxygen concentration in the cathode products. The titanium electrorefining process performed best when the anodes did not contain more than 0.5 pct O, although the anode dissolved with alloys containing up to 25 pct O.

An investigation was initiated to determine the electrorefining characteristics of alloys of titanium and oxygen using an NaCl electrolyte with 4 pct soluble titanium as $TiCl_2$. Tests indicated that electrorefining a titanium-oxygen alloy containing up to a few percent oxygen results in the formation of two titanium-oxygen alloys. The alloy deposited on the cathode has a lower oxygen content than the anode. The other alloy forms as a layer or scale on the anode and has an oxygen concentration up to a maximum of about 14 wt pct. At 14 wt pct O, the rate of cathodic deposition equals the rate of anodic dissolution.

Electrorefining tests using titanium-nitrogen alloys as anode material (*120*) showed that no significant quantity of nitrogen was transferred to the cathode deposit. The nitrogen remained in the anode scale, and the titanium-nitrogen alloy was anodically insoluble in the electrolyte when the nitrogen concentration reached 11 wt pct. The NaCl electrolyte contained 10 wt pct $TiCl_2$. Electrorefining studies in a $LiCl-KCl-TiCl_2$ electrolyte at 480° C with a nitrogen atmosphere, gave deposits with a Brinell hardness of 75 to 85, but the current efficiencies were low.

10,000-A Cell

Before the prototype cell could be operated on a continuous basis to obtain cost data, it was necessary to determine optimum electrolytic conditions. Variables were electrolyte composition, temperature, time of deposition, ratio of anode to cathode area, and current density.

The optimum electrolyte composition of 87.5 pct NaCl and 12.5 pct $TiCl_2$ had been fairly well established in previous small-scale tests. As previously discussed, a relationship exists between the amount of soluble titanium present in an electrolyte and the maximum cathode current density that will produce high-purity metal. Based on this consideration, the soluble titanium content of the electrolyte was held between 4 and 5 pct.

The operating temperature of the cell was limited by the freezing point of the electrolyte and the structural strength of the mild steel used in construction of the equipment. The melting point of an electrolyte containing 5 pct soluble titanium is 770° to 780° C. As stated previously, the creep strength of mild steel is very low at 850° C. It is therefore desirable to keep the temperature of the electrolyte as close to the freezing point as possible. A temperature of 830° to 870° C was used in all work with the prototype cell.

Current density is another very important variable since it affects crystal size, dragout, capital cost, and power consumption. Before any continuous runs were made, the cell was operated at various current densities while other variables, including the total number of ampere-hours, were kept constant. Table 42 shows the average results from 24 tests that were made to establish the effect of cathode current density on the production characteristics. The test results shown in table 42 indicate that an initial cathode current density of approximately 1,000 A/ft^2 (8,000-A dc input) gave the best results. This density was used in all subsequent tests. Power consumption for heating plus electrolysis reached a minimum at 9,000 A. With dc current of that magnitude, the energy required to maintain an operating temperature of 850° C was supplied almost entirely by the electrolysis current.

Deposits formed at cathode current densities of 500 and 750 A/ft^2 contained larger crystals but also had a greater proportion of fines. At 1,000 A/ft^2, the crystal size was very uniform. In all of the tests, the high rate of crystal growth in relation to the rate of nucleation caused the titanium to deposit in a dendritic form that was relatively easy to strip. Titanium occurs in two crystal forms. At about 882° C, the hexagonal close-packed alpha structure changes to a body-centered cubic (beta) crystal. The deposits consisted largely of six-sided crystals of alpha titanium, indicating that the alpha-beta transition temperature had not been reached at the cathode during electrolysis. The uniformity of the deposits from top to bottom of the cathodes demonstrated the excellent throwing power of the bath.

Leaching of cathode deposits was also investigated, since leaching is an important part of the electrorefining process. Large-scale leach tests using agitation times of 0.5, 1, and 2 h showed the 1-h period to be adequate. In the 0.5-h test, the cathode deposits were not completely broken down into individual crystals, and the results in the 2-h test were no better than in the 1-h test. To determine the effect of acid concentration, cathode deposits were leached for 30 min with 5, 10, 15, 20, and 25 vol pct concentrated HCl in water. The leach time was deliberately short to bring out differences in the rate of disintegration. Acid concentration had little effect on either the rate of disintegration or the purity of the metal produced. Another series of tests indicated that acid concentration had little effect on metal recovery. It was concluded that only enough acid need be used during leaching to prevent hydrolysis of subvalent titanium compounds.

The cost of electrorefining offgrade Kroll sponge was determined to be $0.84/lb from data obtained during continuous operation of the prototoype cell for 10-day periods. Enough metal was produced in this time to permit a realistic evaluation of cell performance. One 20-day operation also was made to confirm cost data and to determine the effect of prolonged operation.

Total weight of all deposits produced during the first 10-day run was 1,965 lb. The weight of refined metal remaining after leaching was 1,190 lb. The difference, 675 lb, represents electrolyte removed with the deposits. A screen-size analysis of a 364-lb sample of refined metal from this run is given in table 43.

The cost of electrorefining offgrade sponge was reduced to $0.52/lb in the second 10-day cycle by using 4-in-diam cathodes instead of 6-in-diam cathodes. These permitted a greater quantity of metal to be deposited before stripping became necessary. Unit costs for the two periods are compared in table 44. Both labor and helium

Table 43.—Screen size and hardness of refined metal from first 10-day period

Tyler screen size, mesh	Fraction wt, lb	Size distribution, pct	Hardness, HB
Plus 8	21	5.8	89
Minus 8 plus 34	292	80.2	95
Minus 34 plus 84	45	12.4	189
Minus 84	6	1.6	264

Table 44.—Comparison of operation costs, first and second 10-day periods, cents per pound of metal produced

	1st period	2d period
Labor	46	27
Power, dc and ac	5	4
Dragout	4	2
Helium	19	10
Processing	8	7
Utilities	2	2
Total	84	52

Table 42.—Effect of cathode current density on cell operation

dc input			ac input,	Total power consumption,	Plus 34-mesh fraction		Current efficiency,	Drag-out,
A	V	kW·h	kW·h	kW·h/lb	pct of deposit	HB	pct	pct
4,000	2.3	56	238	10.0	69.6	93	62.4	40.0
6,000	3.5	85	112	7.0	80.1	86	62.8	32.7
8,000	4.6	109	68	5.7	84.9	82	65.9	22.9
10,000	5.7	135	16	5.1	84.0	88	63.0	24.0

costs were drastically reduced by the use of a greater number of ampere hours per deposit. However, since current efficiency decreases with increasing ampere-hours, any further reduction in cost appeared unlikely.

All tests prior to the 20-day production run had been made at constant amperage. Tests using constant voltage indicated some possibility of producing acceptable metal at slightly higher average current densities. This would in turn permit the use of more ampere-hours per run and might lower costs somewhat. During the 20-day test, the cell was, therefore, operated at a constant 4 V rather than at constant amperage.

The appearance of the refined metal remained excellent for about 10 days of the run when the amperage suddenly dropped. The next nine deposits consisted of very fine, dark crystals heavily loaded with salt. The run was then interrupted for 8 h so that the anode material at the bottom of the cell could be stirred up with a poke rod. This led to an immediate improvement in the appearance of the deposits.

The total weight of all deposits produced was 3,421 lb. After crushing, leaching, washing, drying, and screening, 2,472 lb of metal remained. The difference, 949 lb or 27.7 pct, represents dragout. Deposits were divided into "good" and "bad" lots before processing. Bad lots consisted of the nine deposits noted, plus one that was badly oxidized when a slide valve failed to close properly as the receiver was removed from the cell. Table 45 shows some of the results obtained in the 20-day program.

During the time that the cell was operating properly, 1,708 lb of good metal (100 pct plus 34 mesh, 90 HB) was produced. Results, however, did not approach those attained in small-scale work. In preliminary tests, where greater care could be used, hardnesses as low as 66 HB were commonplace. However, in continuous operation, simulating possible commercial practices, an average hardness of 80 to 90 HB on the plus 34-mesh fraction was the best that was produced.

Table 45.—Results obtained in 20-day period

		Bad metal	Good metal
Total weight of deposits	lb	945	2,476
Weight of contained salt	lb	473	476
Weight of refined metal	lb	472	2,000
Dragout ratio	pct	50.0	19.2
Amount of plus 34-mesh metal	pct	68.3	85.4
Hardness of plus 34-mesh fraction	HB	140	90

Table 46.—Analyses of titanium before and after electrorefining, 20-day period, percent

Element	195-HB feed	90-HB product
C	0.10	0.02
Cl	.17	.04
Fe	.08	.01
H	.002	.003
Mg	.14	.008
N	.032	.002
Na	.002	.022
O	.119	.034
S	.008	.001
V	.02	.005

Table 46 indicates the degree of purification attained when the cell was operated continuously over a 20-day period using offgrade Kroll sponge with a Brinell hardness of 195 as the anode material. The "product" was representative of all the plus 34-mesh refined metal. When the cell was operated at an initial cathode current density of 1,000 A/ft^2, approximately 85 pct of the metal produced was coarser than 34 mesh. The minus 34-mesh material was usually recycled to the cell.

CHAPTER 9.—ELECTROWINNING OF TITANIUM CHLORIDES

In 1961, with 10 yr of progressive electrorefining experience as a base, a project was started at the Bureau of Mines Boulder City, NV, laboratory to investigate the electrowinning of high-purity titanium metal from $TiCl_4$. This project continued through 1970.

EARLIER WORK

By the time the results of this work were published (*122*) several other investigators had reported on their research in this field.

Sibert and Steinberg (*186*) presented an excellent review of electrolytic titanium recovery processes together with the work done at Horizons, Inc. They concluded that the process type with greatest commercial potential would be a halide process.

Two papers by Alpert (*1-2*) describe processes using a diaphragm cell with a silica liner, but give no data on the purity of the product, except that titanium with a hardness of 110 HB was produced. An operational cycle was used wherein the Ti concentration was increased to about 4 pct, then stripped out to 0.5 pct.

Opie (*152-154*) and Reimert (*177*) describe methods for the introduction of $TiCl_4$ into a basket-type cathode where the titanium was electrowon and deposited inside the basket. By this procedure, they were able to operate the cell without a diaphragm. However, this process allowed the $TiCl_4$ feed to react with the electrodeposited titanium metal, which resulted in an undesirable powdery metal.

Head (*86*) operated a cell with an atmosphere of hydrogen and $TiCl_4$ to produce a sintered titanium deposit on the end of a cathode that just touched the surface of a molten salt; however, the deposited metal was impure.

Rand and Reimert (*172*) gave a detailed description of a laboratory cell wherein $TiCl_4$ was dripped onto a molten salt. Their cell gave reproducible results, and they recommended a buildup and stripping cycle similar to that used by Alpert. The cathode in their cell was constructed in such a manner that the cell had to be removed to recover the deposit. The procedure of dripping the $TiCl_4$ onto the molten-salt surface resulted in $TiCl_4$ vapors in the atmosphere above the electrolyte that condensed in the cold parts of the cell, causing undesirable operational and corrosion problems. Their best metal, with a hardness of 70 to 93 HB, was produced only during the stripping phase of the operational cycle. The deposits formed during the feed period had a hardness of 130 HB.

Development efforts were made from 1956 to 1968 on the basket cathode cell by Titanium Corporation of America in Henderson, NV.

BUREAU OF MINES INVESTIGATIONS

A thorough study of past work (*122*) indicated that the use of a diaphragm-type cell was the most promising procedure for the electrowinning of high-purity titanium from $TiCl_4$.

A LiCl-KCl-$TiCl_2$ electrolyte was chosen for the initial Bureau investigations because it could be used at temperatures from 400° to 800° C, thus allowing study of a wide range of operating conditions. This electrowinning study was restricted to cells using an Al_2O_3 diaphragm and was designed so that the chlorine produced was exhausted without coming into contact with the metal cell structures. Titanium tetrachloride was fed continuously below the melt surface, which made it possible to maintain a constant composition of the electrolyte. A helium or argon atmosphere was used in the cell to prevent contamination by air.

Equipment

A schematic drawing of the electrowinning cell and its accessories is shown in figure 77. The molten electrolyte was contained inside a thin-walled iron liner, which was fitted inside the 30-cm-diam cell bottom. Three equally spaced 64-mm-diam openings in the recessed cell top accommodated the anode unit, the $TiCl_4$ feed unit, and the electrodeposition cathode. Slide valves and air locks permitted the movement of the feed tube and electrodeposition cathode in and out of the cell bottom exposure of its contents to the atmosphere. Heat-sensitive areas were water cooled.

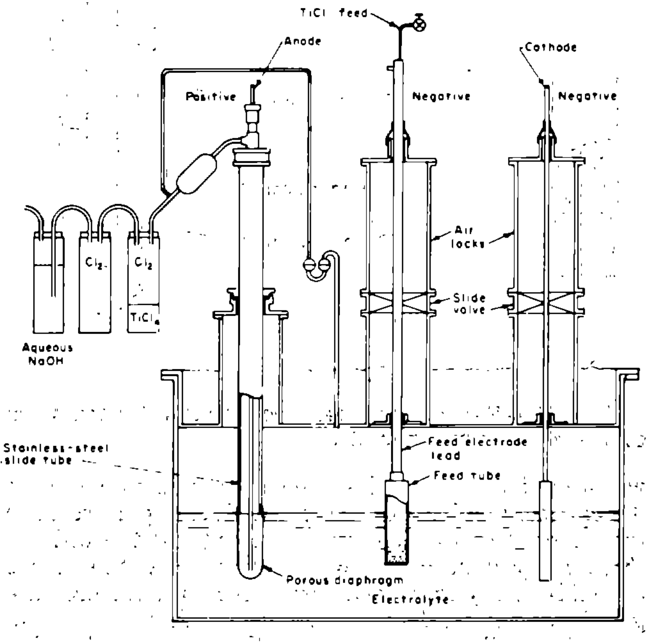

Figure 77.—Schematic drawing of electrowinning cell.

Two essential components of the feed assembly were the water-cooled lead and the feed tube (fig. 78). The water-cooled feed electrode lead kept the $TiCl_4$ in liquid form until it entered the feed tube about 15 to 20 cm above the surface of the electrolyte, then contained the gaseous $TiCl_4$ until it reacted with the $TiCl_2$ in the electrolyte. By this method, the $TiCl_4$ was confined to the inside of the feed tube and no $TiCl_4$ escaped into the other parts of the cell.

The anode section consisted of an anode assembly, a water-cooled $TiCl_4$ condenser and graduated receptacle, an anode-to-cell atmosphere-pressure equalizer, and a water-cooled receptacle of aqueous NaOH for chlorine absorption. A diaphragm was attached onto the lower end of a 90-cm length of an impervious ceramic tube, which

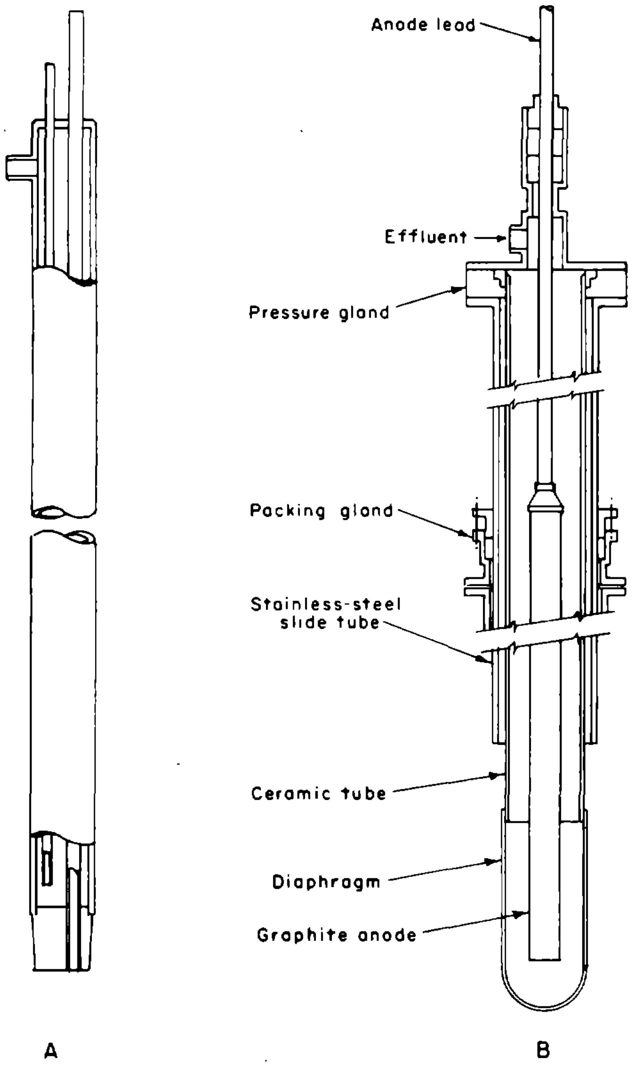

Figure 78.—Water-cooled feed electrode lead (*A*) and cross section of anode assembly (*B*).

was fitted inside a stainless-steel slide tube having a top flange pressure gland for securing and sealing the ceramic tube end. The stainless-steel tube entered the cell top through a packing, which allowed movement of the anode assembly to any immersion depth. Bolted to the pressure gland was the anode assembly lid, which had a central extension with an entrance for the anode lead and a lateral opening for removal of the effluent gases.

Procedure

The electrolyte was a eutectic mixture of LiCl and KCl with $TiCl_2$ added. The LiCl and KCl were mixed and dried before use.

The desired divalent titanium content of the electrolyte was obtained either by reduction of $TiCl_4$ with titanium metal or by electrolytic reduction of $TiCl_4$. In the first method the calculated quantity of $TiCl_4$ was fed into a basket of titanium sponge immersed in the electrolyte. In the second method the calculated quantity of $TiCl_4$ was metered through the feed tube at the rate of 1 mol of $TiCl_4$ per 2F of current.

The electrodeposition cathode was immersed to the desired depth into the electrolyte before current was applied. On completion of a deposition cycle, the cathode and deposit were lifted just above the electrolyte surface and allowed to drain for 1 min. Removal of the deposit from the cell and introduction of a fresh cathode was accomplished through the air locks.

Before the start of each deposition cycle, the water-cooled feed electrode was lowered so that the feed tube was immersed into the electrotype about 10 cm and the $TiCl_4$ feed pump then started. A cathode current of 2 F/mol of $TiCl_4$ was applied to the feed electrode during electrolysis. At the end of the deposition cycle, the $TiCl_4$ pump was stopped and the feed electrode was raised out of the melt. An air lock on this section of the cell permitted the removal of the feed tubes without contaminating the cell atmosphere with air.

The anode and diaphragm were positioned by slowly sliding the assembly through the packing glands (fig. 78B) until the lower end of the ceramic tube was just below the surface of the molten salt. When the anode assembly was replaced, the packing gland was positioned so the diaphram was above the molten salt when the assembly was bolted on the cell, and a flow of inert gas was passed through the cell to purge the assembly.

The cathode deposit was leached with 1 pct HCl solution to remove the electrolyte, after which it was chopped to break up the crystal clusters, washed with distilled water, and dried at 45° C.

Results and Discussion

High-purity titanium was electrowon from $TiCl_4$ fed into a $LiCl\text{-}KCl\text{-}TiCl_2$ electrolyte. The optimum conditions for consistent production of metal with a hardness of 65 to 75 HB were temperature, 520° C; titanium content of the electrolyte, 4.0 pct; average valence of soluble titanium in the electrolyte, 2.0 to 2.1; cathodic current, equally divided between the feed tube and the electrodeposition cathode, and current density at the electrodeposition cathode, 25 A/dm^2. The deposition cycle for a normal run was 3 h with 21 h between cycles. The most critical factor in maintaining product quality was the average valence of the titanium in the electrolyte.

Titanium was deposited on the cathode as closely packed dendritic aggregates or crystal clusters. This type of deposit gave good drainage of the molten electrolyte, and the processed crystals were of a size and shape that should be satisfactory for industrial processing. The analysis of a typical deposit is shown in table 47.

The average cathode current efficiency was 70 pct and anode current efficiency varied from 80 to 90 pct.

Table 47.—Analyses of electrowon titanium, parts per million

Impurities	
O	220
Ba	160
Mn	140
Sr	<80
N	70
Si	<50
Mg	40
Co, Sn	<25
B, Ca, Cr, Fe, V	<20
Al	19
Cu, Ni	<10
Pb	<6
Ag	<5
Mo	<3

Although the melting point of the electrolyte was about 350° C, operation of the cell above 500° C was necessary because of the formation of K_2TiCl_4. This salt complex formed in the anolyte at temperatures below 500° C and separated from the melt as a solid yellow material. The formation of the complex salt also changed the composition of the remaining anolyte and raised the melting point so that the electrolytes solidified in the anode compartment and cracked the diaphragm. When operating temperatures were raised much above 550° C, the useful life of the anode diaphragm was reduced.

Metal of satisfactory quality was produced from electrolytes with a $TiCl_2$ content varying from 2.5 to 11 pct. The electrolytes containing the highest percentages of soluble titanium yielded larger crystals of metal with a slight reduction in salt dragout.

The major design material problem associated with electrowinning in this type of cell was the development of the anode diaphragm. This problem was not satisfactorily solved during the investigation. Theoretical considerations indicated that Al_2O_3 would be as suitable as any other commercially available porous ceramic material, and anode diaphragm durability tests were limited to this material.

Two factors that were identified as affecting diaphragm life were the temperature of the electrolyte and the current applied to the cell, or the anode diaphragm current density. The maximum number of cycles obtained on any diaphragm was 28 when the cell was operated at 520° C. Diaphragms used at 550° C usually lasted for 10 to 15 cycles. In tests where the cell current was doubled to 72 A, the average life of the diaphragm was reduced to six cycles, which indicated that the current-carrying capacity of the diaphragm was an important factor.

Optimum conditions for the electrowinning of titanium from the LiCl, KCl, $TiCl_2$ electrolyte using a $TiCl_4$ feed were established as follows:

1. Titanium content of the electrolyte, 2 to 4 wt pct.
2. Average valence of titanium chlorides in the electrolyte, 2.0 to 2.1.
3. Temperature, 500° to 550° C.
4. Electrodeposition cathode current density, 10 to 50 A/dm^2.
5. Anode current density, 50 to 100 A/dm^2.
6. Diaphragm current density, 15 A/dm^2.

By operating with these conditions, high-purity titanium with a Brinell hardness of 70 was consistently produced.

Evaluation of Diaphragm Materials

Equipment

A 12-in-diam cell with three top openings was used to evaluate various diaphragms (*36*). The cell was similar to one described earlier in this chapter and contained approximately 60 lb of $LiCl\text{-}KCl\text{-}TiCl_2$ electrolyte. Anodes were made of 0.75-in-diam graphite rods placed inside the porous diaphragm and 0.25- to 0.5-in-diam iron rods served as cathodes. Diaphragms studied were 2-in OD by either 4 long or 7.5 in long.

A larger cell contained 300 lb of electrolyte and was used to establish optimum operating conditions. This cell was equipped with four openings, as shown in figure 79. The cathode openings were 4 in. in diameter and equipped with air locks so the deposits could be removed without allowing air to enter the cell.

A 6-in-diam opening without an air lock was used for the anode assembly. Figure 80 shows this anode assembly, which had a 1-in-diam graphite anode and used a 3-in-diam alumina-silica diaphragm 18 in long. The diaphragm was fitted inside the ceramic exhaust tube and sealing to the exhaust tube was not required. About 10 in of the diaphragm was exposed to the molten salt.

Direct current for the electrolysis was supplied by two rectifiers so the deposition current and the feed tube current could be regulated independently.

Operating Procedure

Electrolytes were prepared as previously described and were operated at 520° C. The $TiCl_4$ was pumped through a water-cooled electrode to a molybdenum-lined nickel feed tube immersed in the molten electrolyte. This feed tube was operated cathodically using approximately 2F/mol, which reduced the $TiCl_4$ to $TiCl_2$. Electrowon titanium metal was then collected on a cathode using an equal current. Chlorine gas was produced on a graphite anode and was exhausted from the cell through a ceramic tube that held the diaphragm in place.

Initial studies were made in the 12-in-diam cell using a cell current of 10 A for the 4-in-long diaphragms and 15 A for the 7-in-long diaphragms.

The larger cell containing 300 lb of $LiCl\text{-}KCl\text{-}TiCl_2$ electrolyte was used to study the current-carrying capacity of the diaphragm during continuous operation. This cell had two cathode openings so one cathode could be removed and processed while the other deposit was being formed. Titanium tetrachloride feed rates were adjusted so that the total feed per day was equal to the total titanium metal plus the $TiCl_4$ removed from the cell per day.

Cathode current was divided and equal current was applied to the electrodeposition cathode and to the feed tube. Anode gases and electrodeposit processing were the same as for the smaller cell.

Results and Discussion

The refractory oxides used for cell diaphragms slowly reacted with the $LiCl\text{-}KCl\text{-}TiCl_2$ electrolyte, and their titanium content increased as the immersion time increased.

Alumina containing approximately 12 wt pct silica was used as a standard diaphragm and other materials were compared with it for evaluations. These alumina-silica diaphragms contained approximately 10 pct Ti after being immersed in the electrolyte for 150 h, as shown in table 48.

As the immersion time was increased, the diaphragms became better electrical conductors and were less effective as diaphragms. Electrically conducting materials, such as graphite, act as bipolar electrodes and will not operate as diaphragms. Therefore all materials that contained over 30 wt pct Ti after 150-h immersion in the electrolyte were considered unsuitable for diaphragms. Later tests proved this to be a valid assumption because chemical analysis of the used diaphragms showed they contained less than 30 wt pct Ti when they became inoperative.

Results, as indicated in table 48, showed that the possible diaphragm materials were limited to Al_2O_3 and 12 pct SiO_2, ThO_2, ZrO_2, MgO, porcelain, Al_2O_3, BN, and

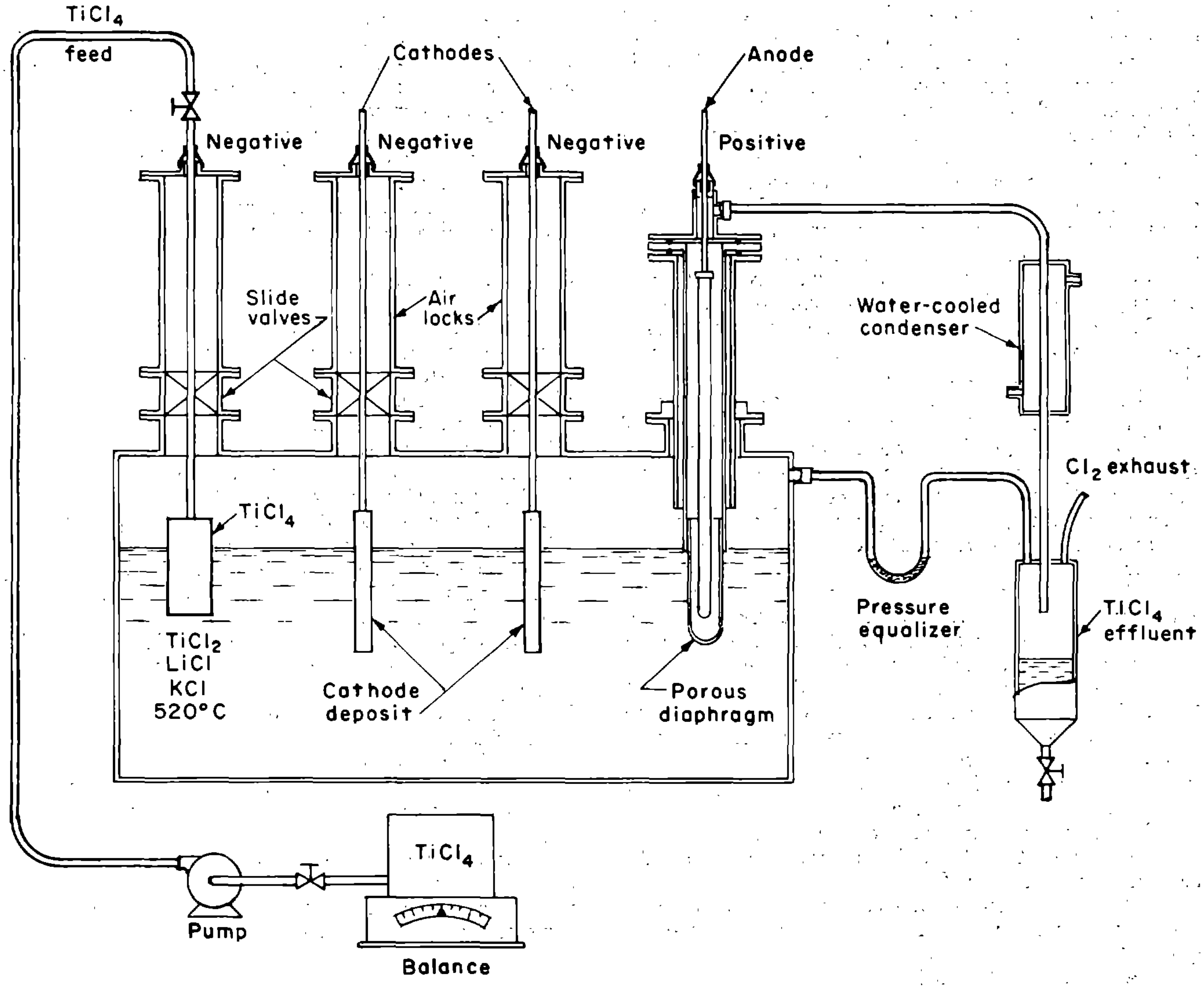

Figure 79.—Twelve-inch-diameter electrowinning cell.

SiO_2. BN and SiO_2 could not be obtained as a porous material of usable thickness and were not tested as diaphragms. Beryllium oxide was used because of its known stability.

All the refractory oxide diaphragms initially tested produced chlorine at the anode. Data from these tests are shown in tables 49 and 50. The short diaphragms used to obtain the data in table 49 were operated with a cell current of 10 A. High currents caused electrolyte depletion inside the diaphragm. The cell current was increased to 15 A to compare results with those of the larger diaphragms of table 50.

Data in table 49 show that for a given set of conditions the Al_2O_3-12 pct SiO_2 diaphragm could be expected to operate for 960 A·h before there was a serious decrease in the anode chlorine efficiency. The anode chlorine efficiencies in table 49 show BeO, ThO_2, and MgO were superior; however, none of them doubled the expected life. Cost, radioactivity, and toxicity problems were factors against the use of ThO_2 and BeO. The MgO occasionally showed corrosion at the salt level and was eliminated on this basis. The reason for this attack was not determined.

In the next series of tests, shown in table 50, the standard Al_2O_3-12 pct SiO_2 diaphragm was compared with pure Al_2O_3 and porcelain. Again, the improvement resulting from use of the two new diaphragms was small. The Al_2O_3-12 pct SiO_2 diaphragm was chosen to establish optimum conditions for the electrowinning of titanium from $TiCl_4$ because none of the other materials was sufficiently superior to justify their added cost and because the Al_2O_3-12 pct SiO_2 was available in a variety of shapes and sizes suitable for an optimizing study.

The improved life of the diaphragms used in table 50 over those used in table 49 was attributed to the lower diaphragm current density. Results of later tests (table 51) confirmed these data.

Diaphragm units constructed as shown in figure 81 were the most satisfactory. Other methods of attaching the diaphragm were with cements, with refractory fiber packing, and by placing the diaphragm on the outside of the ceramic tube. With the diaphragm fitted loosely inside the ceramic exhaust tube it could be easily removed and replaced, while other methods of attachment required leaching in acid to loosen the diaphragm.

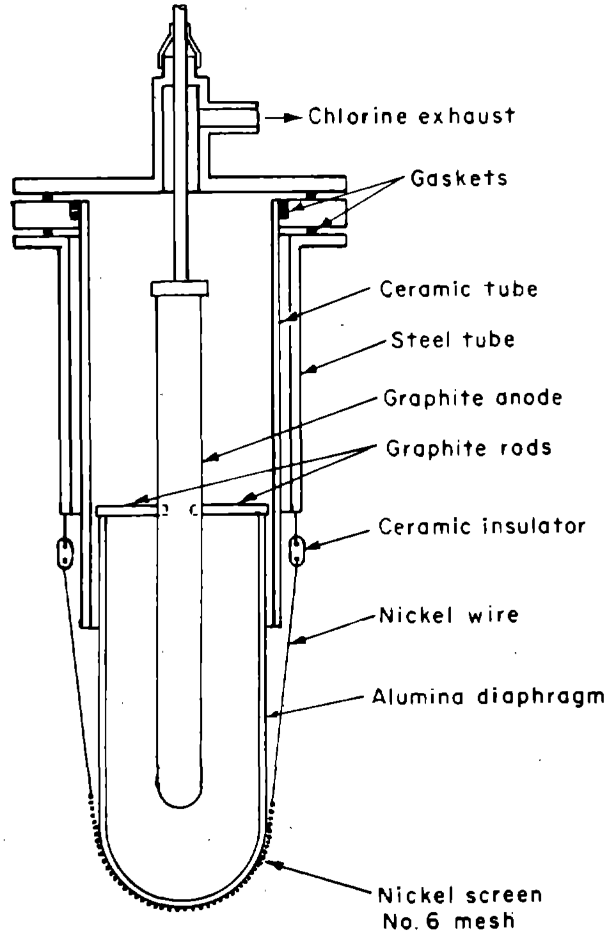

Figure 80.—Anode assembly.

Table 48.—Titanium content of various diaphragm materials immersed in the $TiCl_2$-LiCl-KCl electrolyte at 520° C for 150 h, weight percent

Material	
Al_2O_3 and 12 pct SiO_2[1]	10
ThO_2	10
ZrO_2	10
MgO	10
Refractory paper	50
Asbestos	70
Pyrex glass (frit fine)	40
Porcelain	6
CaF_2	([2])
[3]Al_2O_3	7
Graphite[3]	4
[3]BN	3
[3]TiO_2	70
[3]SiO_2	4

[1] 1,500-h immersion time gave 20 pct Ti content.
[2] Dissolved.
[3] Granular minus 60- plus 80-mesh material.

Table 49.—Effect of electric current of operation on anode chlorine efficiency of titanium electrowinning cell using 2-in-OD by 4-in-long diaphragm, percent[1]

Charge,[2] A·h	[3]Al_2O_3	BeO	ThO_2	ZrO_2	MgO
240	62	61	63	73	69
480	72	70	66	52	88
720	67	73	48	38	75
960	72	66	40	15	73
1,200	23	65	46	ND	69
1,440	ND	74	53	ND	58
1,680	ND	57	ND	ND	50

ND Not determined.
[1] Average anode efficiency from duplicate tests.
[2] Cell current 10 A.
[3] Contained about 12 wt pct SiO_2.

Table 50.—Effect of electric current of operation on the anode chlorine efficiency using 2-in-OD by 7.5-in-long diaphragm, percent[1]

Charge,[2] A·h	Al_2O_3		Porcelain molded
	Slip cast[3]	Flame sprayed	
360	86	99	74
720	75	99	84
1,080	88	91	77
1,440	ND	74	98
1,800	ND	ND	91
2,160	65	76	ND
2,520	69	67	92
2,880	67	85	ND
3,240	62	59	ND
3,600	61	78	72
3,960	ND	62	ND
4,320	ND	ND	73

ND Not determined.
[1] Average anode efficiency for duplicate tests.
[2] Cell current 15 A.
[3] Contained approximately 12 wt pct SiO_2.

Table 51.—Effect of diaphragm current density and electric current of operation on electrode efficiency of titanium electrowinning cell, percent

Charge, A·h	120 A/ft²		60 A/ft²	
	Cathode	Anode	Cathode	Anode
2,000	72	62	56	76
4,000	69	63	63	62
6,000	68	71	63	66
8,000	64	72	59	68
10,000	60	75	68	68
20,000	57	32	69	57
22,000	55	[1]31	62	58
30,000	ND	ND	60	46
40,000	ND	ND	54	42
50,000	ND	ND	51	42
60,000	ND	ND	48	41
66,000	ND	ND	41	[1]22

ND Not determined.
[1] Diaphragm broke.

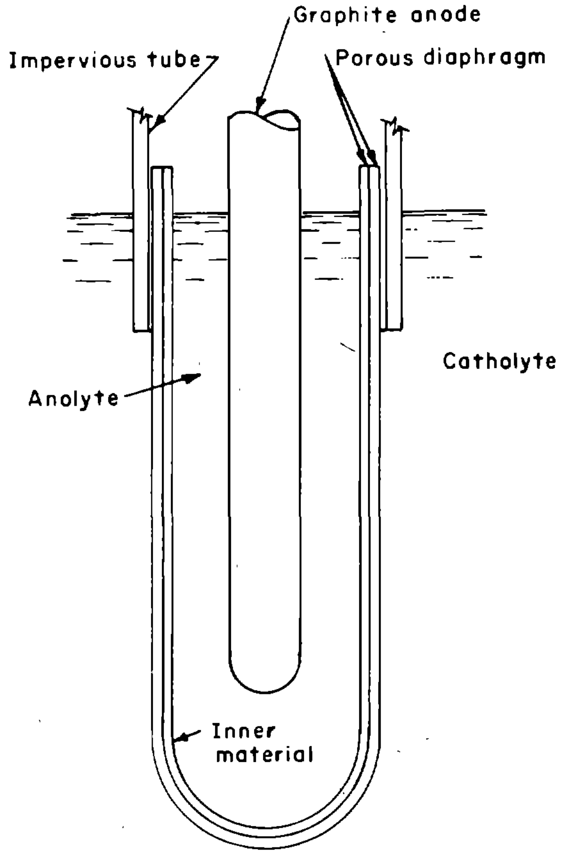

Figure 81.—Solid-material composite diaphragm.

Data from tables 49 and 50 show that materials other than the Al_2O_3-12 pct SiO_2 that have potential value are porcelain, magnesia, and flame-sprayed alumina.

Diaphragm-type cells as described are most useful to produce high-purity titanium. Their major limitation is the low current-carrying capacity and limited life of the diaphragms. A very large diaphragm would be necessary for high production rates.

Composite Diaphragms

The same 12-in-diam cell and operating procedures described previously were used in an investigation of composite diaphragms (*121*).

To utilize and incorporate the desirable properties of each of two-component or more materials for the diaphragm structure, the composite diaphragms represented by figures 81 and 82 were constructed and tested. Composite diaphragms depicted by figure 81 utilized one of the proven solid diaphragm materials or an Al_2O_3 refractory cement coating as the inner dielectric structure proximate to the anolyte, and a tightly fitting porous metal or other material for the outer structure proximate to the catholyte. Composite diaphragms that utilized both solid and loose materials in their structure are depicted by figure 82, in which the loose material is contained between solid inner and outer structures. The size and form of the cylindrical composite diaphragm were determined by the characteristics of the structural materials; in general, the dimensions varied from 2- to 3.5-in OD, 8- to 12-in length, and with wall thicknesses of 1/16 to 3/4 in.

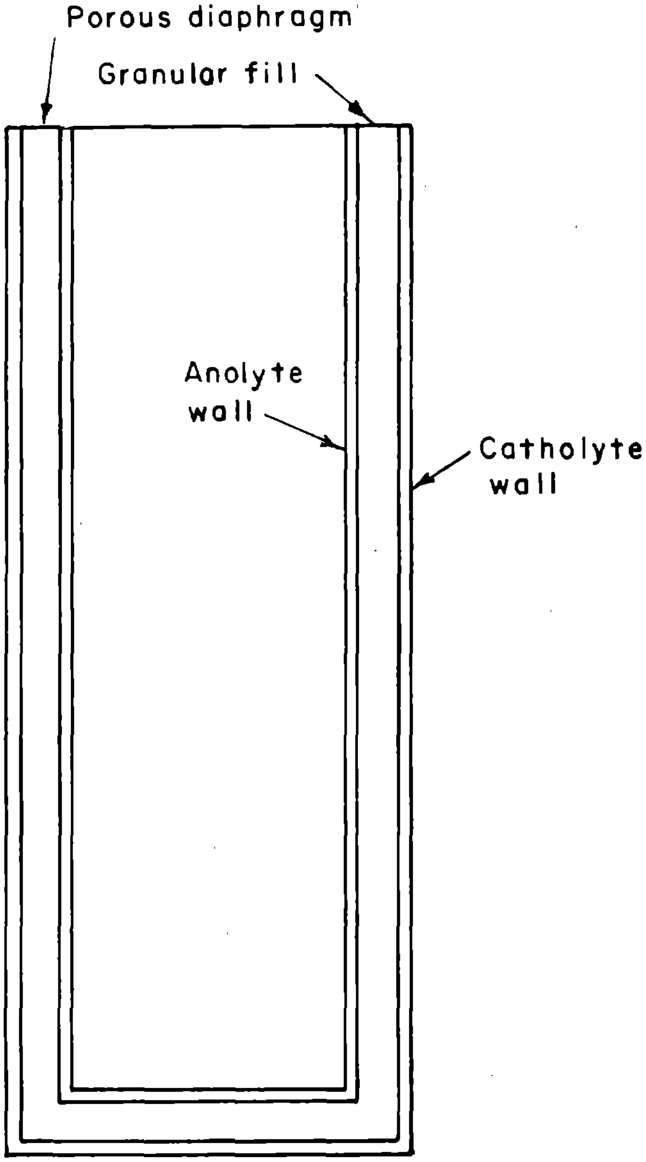

Figure 82.—Loose-fill-material composite diaphragm.

Solid-Materials Composite Diaphragms

Shown in table 52 are the diaphragm descriptions and test data on the solid materials composite diaphragms that were made and tested.

The highest chlorine efficiencies, 100 pct, were obtained with the 12- and 25-µm-porosity graphite diaphragms with an inner cement coating (diaphragms 7 and 10). This type was, however, subject to the same current density limitation as the porous ceramic diaphragms.

Loose-Fill-Materials Composite Diaphragms

Data from six loose-fill-material composite diaphragms are shown in table 53. Alumina granules, silica sand, and boron nitride fibers were the loose materials used to fill the diaphragms. To retain the loose granules, the support contiguous to the catholyte was made of 80-mesh nickel screen. A 30-µm-porosity alumina diaphragm was used for the liner of diaphragm 13, and the liner for diaphragm 14 was a 20-mesh nickel screen coated with cement. To attain a greater porosity, the screens of diaphragms 15 and 16 liners were coated with a mixture of two parts Alundum-60 (approximately 60 mesh) granules and one of cement.

The properties of strength, flexibility, resistance to corrosion, low replacement of titanium in loose materials, and ability to tolerate high current densities were attained in the composite loose-fill-material diaphragms. These were improvements over the diaphragms described by Couch (*36*) and Leone (*121*). Sand would be the most economical fill but would still require replacement, as shown by the 4-pct Ti content that resulted in tests. The 1-pct Ti replacement that occurred in the BN fibers fill was highly favorable and could likely be lowered by the use of granular BN; however, the cost is high. The low 0.2- to 1.0-pct Ti replacement in the alumina-granular fill favors this as the preferable fill.

RECENT WORK

Cobel, Fisher, and Snyder (*31*) reported on a high-purity electrolytic titanium pilot plant being operated by the D-H Titanium Co. (Dow Chemical and Howmet Turbine Components Corp.). The technology is an outgrowth of the work originating at the Bureau of Mines Boulder City (NV) Research Center (*121-122*). Prototypes were operated in a single anode 5,000-A cell producing 45 kg/d of metal (99 lb/d). Construction of an industrial-scale multiple anode cell was planned for a demonstration plant of 1 Mkg/yr of metal (2.2 MMlb/yr).

Cell operation was demonstrated at temperatures from 520° to 600° C using an electrolyte composed of KCl

Table 52.—Test data on composite diaphragms constructed of solid materials

Diaphragm[1]	Construction material	Porosity, µm	Wall thickness, in	Current, A·h	Anode Cl_2 efficiency, pct
1	Cement on Ni wire mesh	NAp	0.06	200	70
2	Flame-sprayed Al_2O_3 with Ni screen cover	NAp	.06	2,700	56
3	..do	NAp	.13	2,300	65
4	Porous stainless steel and cement	5	.06	1,000	25
5	..do	100	.06	850	15
6	Porous nickel and cement	20	.13	4,100	74
7	Porous graphite and cement	12	.75	720	100
10	..do	25	.75	1,100	100
11	..do	25	.50	3,790	60

NAp Not applicable.

[1] Diaphragms 8 and 9 omitted owing to mechanical failure; diaphragm 12 was nonfunctional.

with 45 to 60 pct LiCl and $TiCl_2$ feed. Titanium concentration in the electrolyte was 1.5 to 3.5 pct.

Several patents have been issued to Dow Chemical Co. on cathode design, diaphragms, reduction apparatus, and reduction methods (*24, 98, 100-101*).

The demonstration plant was constructed and operated with a five-anode cell at 25,000 A. The process was deemed fully satisfactory, but the project was terminated before a commercial plant was built. Termination was decided on the basis of economics and the titanium market, which peaked in 1981. A poor payoff was predicted because of dropping titanium prices (*143, 207*).

Table 53.—Test data on composite diaphragms constructed of cement-coated nickel screen with loose-fill material

Diaphragm[1]	Mesh size and fill material	Current, A·h	Anode Cl_2 efficiency, pct
13	Alundum-60	6,000	55
14	..do	12,600	70
16	Alundum-120	7,500	71
17	Minus 80- plus 100-mesh SiO_2	2,200	99–30
18	..do	4,400	65
19[2]	BN fiber	5,000	70

[1] Diaphragm 15 omitted owing to excessive permeability.

[2] Wall thickness was 0.5 in, all other diaphragms had a 0.25-in-thick wall.

CHAPTER 10.—ANALYTICAL METHODS[7]

When the Bureau of Mines started its research on titanium in 1938, the only methods available for analyzing the starting materials and the products were the standard textbook wet chemical procedures. Rapid high-precision instrumental analysis with low recognition limits was in its infancy. Coincidental with the research on production methods and fabrication techniques, a continuous research effort was expended in the development of quantitative analytical procedures. Objectives were to obtain the most rapid and least costly methods consistent with accuracy and precision requirements for process control and control of product quality. The methods used changed at intervals as new analytical instrumentation became available and as process and product improvements required analyses of higher accuracy and lower recognition limits.

The major research on analytical methods was on the analysis of contaminants in metallic titanium. Development of methods for determining impurities in $TiCl_4$ and titanium lower chlorides in NaCl were also a part of the research effort. Hardness was used as a major criterion of metal quality. Equipment and methodology for rapid and precise determination of the Brinell hardness number was developed that was generally adopted by industry for hardness determinations of titanium sponge.

Because of experience and expertise developed in titanium sponge analysis, the Bureau was selected by the General Services Administration (GSA) as the official laboratory for testing all metal procured by the U.S. Government under the GSA revolving inventory fund and under production contracts resulting from the Government-sponsored titanium expansion program.

SAMPLING PROCEDURES

The problems associated with obtaining a representative sample of a metal were aggravated in the case of titanium metal. In all of the reduction processes, the metal was formed in the solid state and was inherently nonhomogeneous. The physical features of the metal as produced by active metal reduction of the tetrachloride militate against obtaining a truly representative sample. First, the mechanism of the reaction resulted in the formation of metal of varying quality at different times in the reaction cycle and at different locations in the reaction vessel. Second, the removal of the reaction mass resulted in various-sized pieces of metal, with a tendency for impurities to be concentrated in the smaller sizes. Therefore, because the larger pieces were the purest and thus the most malleable, it was not possible to reduce them to a size that permitted satisfactory blending and sampling.

The procurement of a sample from a molten stream or from programmed sampling of an ingot cast from a molten mass was not possible in the case of titanium because of the reactivity of molten titanium and the contamination that was introduced in a melting procedure.

Although the problem of obtaining a representative metal sample was never completely solved, a procedure was developed that produced an acceptable sample. Each lot of metal to be sampled was blended, usually in a cement mixer type blender, and a portion of 100 lb or less was withdrawn for further sampling. The withdrawn portion was split in a riffle to provide a 250-g fraction for impurity analyses and three 80-g fractions for melting and hardness testing. The 250-g sample was pressed into a 2.25-in-diam compact at 15 tons/in^2.[8] The compact, which was about 1.25 in thick, was turned in a bench lathe to form chips representing 60 pct of the weight of the compact, 30 pct from each face. The chips were combed with a magnet to remove tramp iron.

The chips formed in the turning operation varied in size, and the impurities continued to be concentrated in the fines. The harder and less pure the metal, the larger the proportion of fines produced in the sample. One- to ten-gram portions were used in the various analytical procedures. The most satisfactory method for obtaining the weighed sample was to roll the chips briefly on glazed paper, spread them evenly, and take a series of evenly spaced dips to the surface of the paper with a spatula. A microsplitter was tried for cutting out the sample, but when the weighing was done by an experienced analyst, the added time required was not justified.

The 80-g fractions were pressed in 2.25-in-diam wafers, which were melted into small ingots. Turnings from these ingots were sometimes used for analytical samples, but the problems of sample inhomogeneity continued, although to a lesser degree for some elements.

Samples of $TiCl_4$ were obtained by cutting a fraction from a flowing stream into a dry sample container that was sealed until further sampling was required. Because corrosive fumes formed immediately upon contact of $TiCl_4$ with the atmosphere, most analytical samples were taken by pipette and the analysis expressed in grams per liter. Admittedly, the volumetric sampling was not exact, as the $TiCl_4$ had a specific gravity and viscosity unlike that for which pipettes are calibrated. However, the impurity concentrations in the tetrachloride were normally so low that error in measuring the sample volume did not affect accuracy significantly, and the use of consistent pipette delivery techniques resulted in reproducible results. For analyses that required weighed samples, the $TiCl_4$ was introduced into a glass ampoule that was sealed with a rubber cap. The empty ampoule was weighed with the rubber cap in place, $TiCl_4$ was added by use of a medicine dropper, the cap was replaced quickly, and the ampoule was reweighed.

The difficulties associated with sampling of chloride salt byproducts and intermediate products were caused by the hygroscopic nature of the salts. On the salts for which valence state determinations were made, special handling was necessary to prevent sample oxidation. The availability of the dry room required for the process provided the necessary environment for sampling the salt products. When use of the dry room was not convenient, the samples were prepared in dry boxes. In preparation for valence determinations, the samples were crushed to minus 8 mesh with frequent screening to minimize fines. When analysis was made for indicated titanium, the minus 65-mesh fraction, not to exceed 10 to 15 pct, was discarded because of the possibility of excessive oxidation of the fines. When samples containing over 30 pct indicated titanium were analyzed, crushing under an inert atmosphere as well as discarding of fines was required to prevent low results caused by sample oxidation.

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[7] By Alick Mackie, research supervisor, Albany Research Center, Bureau of Mines, Albany, OR.

[8] In this chapter, "ton" indicates 2,000 lbf.

CHEMICAL PROCEDURES

The chemical procedures described are not necessarily the most precise or accurate that could be developed, nor are they claimed to be preferred or standard methods. Their reproducibility and accuracy were tested by a large number of determinations and by cross-checks with other laboratories. Selection of the described method was often made because of analytical speed and simplicity consistent with required accuracy. Refinements that gave no appreciable improvement in results were omitted.

Titanium Metal (164, 166)

Chloride

The classical method of precipitation and weighing as AgCl gave the most reliable analysis for chloride in titanium sponge. The common nephelometric method failed to give satisfactory reproducibility. The chloride content of titanium sponge, expressed as chloride, was usually about 0.1 pct.

Nitrogen

A modification of the Allen method for nitrogen in iron and steel was found to be the most suitable chemical method for determination of nitrogen in titanium sponge. The nitrogen content of the sponge varied from 0.003 to 0.03 pct, but most of the samples contained near 0.01 pct.

Sulfur

The method described assumes that all the sulfur in the titanium sponge has been reduced to the sulfide. The normal range of sulfur in titanium sponge was between 0.002 and 0.010 pct. However, samples containing larger amounts of sulfur were analyzed by an evaluation technique where the sulfur was converted to H_2S and collected in an ammoniacal solution of cadmium chloride. After an excess of standard iodine was added, the solution was acidified and the excess iodine was titrated with a standardized solution of thiosulfate. The sulfur content is calculated.

Iron

The colorimetric determination of iron by 1,10-orthophenanthroline ($C_{12}H_8N_2{\cdot}H_2O$) proved very satisfactory. It was used directly on an acid solution of sponge by complexing the titanium with tartrate. Sponge varied from about to 0.05 to 0.25 pct Fe. Results from this method are in agreement with those of the spectrochemical method, which is described in the section on spectrographic procedures.

Special samples contained several percent iron, and these were determined by the common dichromate titration after reduction by stannous chloride ($SnCl_2$). Occasionally titanium would be partly reduced, requiring careful control of the dichromate titration.

Magnesium and Calcium

Magnesium was usually the predominant impurity in magnesium-reduced titanium sponge, varying from 0.3 to 0.5 pct in leached sponge and from 0.07 to 0.2 pct in distilled sponge. (The magnesium and calcium are determined by the standard gravimetric phosphate method, which may be found in any standard text on quantitative analysis.) The spectrochemical procedure, described in a later section, is in agreement with the longer chemical methods.

Manganese

Manganese was a common impurity in titanium sponge, varying in amounts according to the method of production. The concentration range was usually 0.005 to 0.50 pct Mn. A modification of the sodium arsenite ($Na_3AsO_4{\cdot}12H_2O$) method for determining manganese was used. Results obtained by this procedure agreed with spectrochemical determinations.

Silicon

Silicon was a minor impurity in most titanium sponge, usually less than 0.05 pct, and no satisfactory chemical determination in that concentration range was derived. The conventional gravimetric procedure using hydrofluoric acid was satisfactory for metal containing several tenths of a percent of silicon, but in the lower ranges, especially below 0.05 pct, the results were low. All silicon determinations were made spectrochemically.

Vanadium

Most of the sponge analyzed contained less than 0.03 pct V. Spectrochemical methods were usually used for determining vanadium in both sponge and tetrachloride. The peroxide method was satisfactory for wet chemical determination of vanadium.

Molybdenum

Molybdenum was not usually found in titanium sponge. The stannous chloride-thiocyanate colorimetric method for molybdenum was satisfactory on low concentrations in titanium sponge.

Chromium

Chromium was a rare impurity of titanium sponge. Special samples submitted, with a chromium content varying from 0.01 to 10.0 pct, were analyzed. The most satisfactory method was to oxidize the chromium to chromate, add a measured excess of ferrous ammonium sulfate [$Fe(SO_4){\cdot}(NH_4)_2SO_4{\cdot}6H_2O$], and titrate with potassium dichromate ($K_2Cr_2O_7$).

Phosphorus

Phosphorus has not been detected in titanium sponge samples. It may be present in metal prepared by electrolysis from a molten bath. For that reason, several analysis procedures were investigated. For this investigation, phosphorus was added in small increments to phosphorus-free titanium. The most consistent results were secured with the method of Codell and Mikula (*32*).

Tin (200)

Modifications of two methods proved satisfactory for analysis of tin. An iron reduction method was acceptable in the 0.01- to 1.0-pct range, and a lead reduction method was acceptable in the 0.03- to 1.0 pct range.

Columbium and Tantalum

Although columbium and tantalum were not usually found in titanium sponge, these metals were present in some titanium ores; occasional analyses were made to determine the disposition of these impurities. A liquid-liquid extraction followed by gravimetric determination was adopted.

Titanium Tetrachloride

Free Chlorine

The procedure determines not only free chlorine, but all other substances that liberated iodine from acidified aqueous potassium iodide solution. Free chlorine in crude tetrachloride usually ranges from 0.2 to 1.0 g/L; in purified tetrachloride it is usually below 0.1 g/L. The sample is introduced into an iodide solution by the use of an ampoule. The liberated iodine is titrated with a standard thiosulfate solution.

Vanadium

The spectrochemical method is preferred. The chemical procedure was used for crude samples, where the vanadium content is usually 1 to 3 g/L. Properly purified samples contain less than 0.1 g/L, for which the method is unsuitable. Sampling of the $TiCl_4$ using Stoddard solvent and dry ice reduces the danger of losing part of the sample.

Iron

The same ortho-phenanthroline colorimetric procedure that is used for iron in titanium metal is utilized. A bath of dry ice and Stoddard solvent is used to sample the $TiCl_4$.

Silicon

The spectrochemical method is preferred. The conventional method of dehydration with sulfuric acid, described under silicon in the "Titanium Metal" section, may be used for crude tetrachloride containing several tenths of a percent of silicon. Sampling is done by the dry ice and Stoddard solvent technique.

Sulfur

Sulfur in the range of 0.01 to 0.50 g/L is usually found in commercial $TiCl_4$. The method consists of oxidizing the sulfur to sulfate, removing the titanium, and precipitating barium sulfate.

Phosphorus

The phosphorus is precipitated as the phosphomolybdate, which is satisfactory for amounts of phosphorus over 0.1 g/L. The sampling is done using the Stoddard solvent cooled with dry ice.

Nonvolatile Residue

The procedure described here was developed to check the nonvolatile residue content of crude $TiCl_4$, which ranged from 1.7 to 6.1 g/L.

The sample is placed in a platinum boat inside a tube sealed into a water-jacketed condenser. Everything must be absolutely dry. The system is flushed with helium prior to heating. The system is heated slowly until all the tetrachloride is volatilized. Any residue left in the boat is weighed.

Average Effective Valence (27)

The average effective valence (AEV) of titanium compounds, i.e., the proportion of Ti^2, Ti^3, and Ti^4, in partially reduced $TiCl_4$, was an important variable in controlling the quality of product in the sodium reduction of titanium.

Two satisfactory empirical methods were developed for calculating the value for the AEV of soluble titanium in a $TiCl_x$-NaCl salt mixture. Both methods were based on the reducing power of subvalent titanium chlorides; i.e., $TiCl_2$ and $TiCl_3$. In the indicated titanium method, the oxidation of $TiCl_2$ and $TiCl_3$ to $TiCl_4$ is measured, and in the hydrogen evolution method, the oxidation of $TiCl_2$ to $TiCl_3$ is measured. The hydrogen evolution method, applicable only to mixtures having AEV's less than 3.0, is based on the assumption that $TiCl_2$ and $TiCl_4$ do not coexist in a salt mixture.

FLAME PHOTOMETRIC PROCEDURES

Lithium, potassium, and sodium were determined in concentrations from 10 to 1,000 ppm in titanium metal. Samples were dissolved in HCl, diluted to volume, and aspirated into an oxygen-acetylene flame. Intensities of emitted spectral lines of the impurity elements were converted to concentrations by reference to graphs of the intensities of an appropriate series of standards against their concentrations.

SPECTROCHEMICAL PROCEDURES

During the course of the research on analysis methods, three separate spectrochemical techniques were investigated, and satisfactory methods were derived for determination of some of the metallic impurities commonly found in titanium. The three techniques were the rotating disk-solution spark method, the porous cup-solution spark method, and the TiO_2 conversion-dry powder arc method. Because instrument settings and configurations are a function of the particular equipment available to an analytical laboratory, such information is not included in the following description of the research or the procedures developed.

Rotating Disk-Solution Spark Method (164)

Solution techniques were investigated because of two obvious inherent advantages: (1) A comparatively large sample could be dissolved, thus minimizing sampling error caused by heterogenous dispersal of impurities, and (2) standards could be more easily prepared in solution form.

The instrument used for developing and evaluating the rotating disk-solution spark method in the Bureau's laboratories was a three-meter grating instrument with an average reciprocal linear dispersion of 5.5 Å/mm in the first order. Procedures were developed using both a condenser discharge-spark excitation source and a high-voltage air interrupter-type spark source. The electrodes were high-purity graphite: the upper electrode was 0.25 in. in diameter and tapered to a hemispherical point that was reshaped after each exposure, and the lower disk electrode was 0.5 in. in diam and 0.125 in thick. The spectrum was recorded for all determinations on Eastman Spectrum Analysis No. 1 Plates.

The spectral region used for all determinations was 1,870 to 3,290 Å, first order. An 8-A dc arc iron spectrum was used to establish the plate emulsion calibration curve. The characteristics of the emulsion on the plates used were such that one calibration curve was satisfactory for all the wavelengths covered. Deviations are usually less than 10 pct.

The elements in titanium metal for which satisfactory determinations were developed were iron, magnesium, silicon, manganese, vanadium, aluminum, and chromium. Methods for determining vanadium and silicon in $TiCl_4$ were also developed.

Standards for metal analysis were prepared from the purest titanium metal available. The metal was dissolved by adding for each gram of metal, in order, 1.0 g of tartaric acid, 20 mL of distilled water, and 10 mL of concentrated HCl, followed by low heating until all of the metal had dissolved. The solution was made up to volume and divided into appropriate aliquots to which impurity elements were added to cover the desired range. The solutions were then heated to about 80° C and slowly oxidized with dilute nitric acid (1:2); care was taken to avoid more than a drop or two excess of acid. Solutions were then cooled and made up to volume with distilled water.

Stock solutions of manganese, iron, magnesium, aluminum, and chromium were prepared by dissolving high-purity metal in HCl and diluting to concentrations of 1.0 g/L. Silicon stock solution was prepared by dissolving sodium metasilicate (Na_2SiO_3) in distilled water, analyzing chemically for silicon content, and diluting to a 1.0-g/L solution. Vanadium stock solutions were prepared by dissolving ammonium metavanadate (NH_4VO_3) in dilute H_2SO_4, analyzing, and diluting to volume.

Impurities present in the titanium metal used in preparing standards were determined by chemical analysis; however a further check was made by the methods of Harvey (*83*) or Nachtrieb (*137*) for estimating residual impurities from preliminary working curves. Stock solutions of silicon for preparation of standards for anlayzing silicon in $TiCl_4$ were prepared by mixing $TiCl_4$ containing 5.0 g/L Si with $TiCl_4$ containing less than 0.1 g/L Si. Vanadium standards were prepared from the same stock solution used in preparation of the metal standards.

Titanium was used as the internal standard. Suitable lines were found close to the selected element lines to make convenient analytical pairs.

For analysis of titanium metal, 5 g of the sample was dissolved and oxidized in the same manner as described for preparation of standards and diluted to a titanium concentration of 20 g/L. Experience showed that a minimum 5-g metal sample was necessary to minimize the effect of impurity segregation. In the analysis of $TiCl_4$, 5-mL samples were used when the vanadium concentration was 0.1 to 1.0 g/L and 2-mL samples for concentrations of 1 to 4 g/L. The analytical sample or standard $TiCl_4$ was prepared for sparking by adding it dropwise to 50 mL of partly frozen 20 pct H_2SO_4. The cooling technique was necessary to prevent loss of $SiCl_4$ by volatilization. Samples were ready for excitation as soon as they were warmed to room temperature. Silicon results tended to become erratic when the tme interval between preparation and excitation exceeded 12 h.

Porous Cup-Spark Method (166)

A second spectrographic solution technique, which utilizes the porous cup method, was developed at the Bureau's former College Park (MD) Metallurgy Research Center. Research was concerned with titanium alloys as well as with commercially pure metal (sponge); the method was tested over higher impurity ranges than the rotating-disk method. The spectrograph used was of the same basic type as the one used in developing the rotating-disk method.

Agreement between the results of reliable chemical analysis and spectrochemical analysis by the porous cup technique is usually good if the spectrochemical standards are accurately made. Deviations from chemical values are usually ±6 pct or less.

Dry-Powder Method (215)

A dry-powder chemical procedure was developed for 19 impurity elements in titanium metal, oxides, or chlorides in which all samples were converted to TiO_2. The procedure was quantitative for 18 elements, but semiquantitative for beryllium.

The spectrograph used in this procedure was a two-meter dual grating instrument, which gave average reciprocal linear dispersions of 4.02 and 8.21 Å/mm; both dispersions were in the first order. The instrument was equipped with filters that could be used in combinations to give various intensity factors with either or both beams.

For preparation of standards, a TiO_2 matrix material was prepared from the purest available $TiCl_4$ by hydrolyzing, centrifuging, washing, drying, and igniting. The concentration of the residual impurities was determined by the method of Nachtrieb (*137*). Standards were synthesized by mixing the impurity elements, in most instances as oxides, with the TiO_2 matrix material. The 19 elements to be determined were arranged into four groups in such a way as to keep mutual interferences within the standards at a minimum and to permit the segregation of certain elements into a group apart for special treatment. Basic standard samples were prepared for each group. Two buffer diluent internal standard mixtures were made as follows:

Buffer 1.—Equal weights of spectrographic-grade graphite powder and lithium carbonate (Li_2CO_3) plus 0.04 pct Ga [added as gallium sesquioxide (Ga_2O_3)].

Buffer 2.—Equal weights of graphite powder and lithium carbonate plus 1.5 pct Ge [added as germanium dioxide (GeO_2)].

Metal samples were prepared by dissolving approximately 2 g of titanium in 75 mL of HCl, oxidizing with nitric acid, and evaporating the solution to near dryness in a platinum dish. After the sample cooled water was added to the pasty residue to hydrolyze and precipitate the titanium. The sample was then evaporated to dryness and transferred to a cold muffle furnace, and the furnace temperature was slowly raised to 800° C and maintained for 4 h. Titanium tetrachloride samples were prepared by diluting approximately 2 mL of the chloride with four times its volume of pure carbon tetrachloride and adding the mixture to an approximately equal volume of water in a platinum dish cooled in an ice-water bath. The solution was then evaporated to near dryness and processed as for metal samples. Portions of the oxidized samples were mixed (1:1) with each of the buffers, and three electrodes were prepared from each of the two mixes.

The overall precision of the method in terms of the coefficient of variation is 20 pct. Coefficient of variation (v) in this method, is calculated as follows:

$$v = \frac{100}{\bar{x}}\sqrt{\frac{\Sigma d^2}{n-1}},$$

where $\bar{x}$ = average concentration, ppm,
d = difference of the determination from the mean,
and n = number of determinations.

The only beryllium line found, Be 3130.42, practically coincided with a weak titanium line, Ti 3130.38 (arc intensity 2). This fact, confirmed by the shape of the curves, indicated that the determination must be regarded as semiquantitative except at high concentrations of beryllium. This interference made it impossible to determine the residual concentration of beryllium, if any, in the matrix material; therefore, the curve was arbitrarily cut off at 40 ppm.

The silver line, Ag 3280.68 (0.3), showed strong self-absorption at concentrations greater than 45 ppm and was of doubtful value above that point. The same was true of Cu 3247.54 (0.3) above 100 ppm.

Repeatability figures might be improved substantially if a means were found for achieving more thorough mixing of standards without incurring the attendant risk of contaminations. There are indications that the other steps of the procedure are capable of yielding precision values higher than those tabulated.

FUSION PROCEDURES (199)

It was recognized very early in the titanium production research that the impurity element having the greatest effect on ductility was oxygen. At a later date, when titanium alloys were used in highly stressed parts such as turbine blades, it was determined that hydrogen contributed to age embrittlement. Methods for determination of oxygen and hydrogen in small amounts were required, and fusion methods were developed that resulted in evolution of the impurities as gases, followed by precise measurement. Procedures were developed for determining oxygen, hydrogen, and nitrogen by vacuum fusion and oxygen by fusion in an inert gas. Dry-crucible (*213*), platinum-bath (*218*), and platinum-flux (*79*) procedures were investigated.

In 1958, the Laboratory Equipment Corporation, St. Joseph, MI, developed an apparatus that employed an inert-gas fusion technique for determination of oxygen in metals.

A platinum-flux technique was employed in which the samples were wrapped in 10 times their weight of platinum and introduced into an outgassed graphite crucible at 2,475° C.

HARDNESS TESTING (7)

The hardness of titanium was used as a prime indication of its quality, and a rapid, reproducible procedure was developed for making the determination.

Three sample splits of approximately 80 g each were pressed into 2.25-in-diam wafers at a pressure of 8 to 10 tons/in^2. The wafers were loaded into trays that were placed in the air lock of the melting furnace.

Each tray had a capacity of 15 buttons and was loaded in a particular sequence that permitted the melting position of the test samples to be rotated, minimizing any effect of position. The first tray to be used was loaded with 12 test and 3 control buttons distributed in the tray. Additional trays were loaded with 14 test samples and 1 control button. Each side of the button was melted, then a smooth surface machined for testing the hardness.

The control compact was taken from material for which a minimum of 500 buttons had been melted to establish a hardness pattern. A typical control material had the following limits: 95.5 minimum to 99.0 maximum HB. If a control fell outside these limits, the whole set melted with that button was resampled and tested.

CONCLUSIONS

Since beginning with a small-scale effort in 1938, the Bureau of Mines has completed extensive research investigations in all areas of titanium metal production. Many major accomplishments have been achieved.

1. Sufficient titanium resources have been identified in the United States to supply projected needs for titanium metal, and recovery procedures have been demonstrated to develop those resources.
2. Methods have been developed for concentrating titanium from a variety of domestic source materials such as sands containing rutile or ilmenite, massive deposits containing rutile, ilmenite, or perovskite, and mineral processing waste products. Recovery techniques investigated include physical beneficiation, leaching, volatilization, roasting and sintering, and smelting.
3. Technology has been developed to produce titanium tetrachloride ($TiCl_4$) from titanium dioxide materials such as rutile concentrates, synthetic rutile, titaniferous slags, and chlorination process residue; ilmenite; and reduced titanium compounds. Methods have been developed for purifying $TiCl_4$ by chemical treatment to remove metallic impurities followed by distillation to eliminate silicon tetrachloride.
4. Methods have been developed for producing titanium metal in sponge form by reducing $TiCl_4$ with magnesium or sodium metal in batch processes. When sodium was used, two-stage reduction was found to be more effective than single-stage reduction. Sponge metal was purified by hydrochloric acid leaching and vacuum distillation procedures to remove magnesium chloride and unreacted magnesium and by hydrochloric acid leaching to remove sodium chloride.
5. Research by the Bureau on production of titanium sponge metal has led to the commercialization of the Kroll magnesium reduction process.
6. Melting processes have been demonstrated for effectively reducing the chloride content of titanium sponge metal and consolidating sponge and scrap metal. Controlled-atmosphere electric-arc melting, electric-arc slag melting, and induction slag melting techniques were all successfully applied. Methods have been developed for making consumable electrodes from sponge metal for use in the arc-melting processes. The use of water-cooled copper crucibles has become accepted practice in melting reactive metals.
7. The technical feasibility of purifying titanium sponge and scrap metal by electrorefining has been demonstrated. Procedures using molten-salt electrolytes composed of $NaCl\text{-}TiCl_2$ or $NaCl\text{-}K_2TiF_6$ were developed. The refining processes effectively eliminated impurities such as oxygen, nitrogen, iron, and some other metals, but not vanadium or manganese.
8. The potential for developing a process to produce titanium metal from $TiCl_4$ by electrowinning has been shown. High-purity metal was won from a $LiCl\text{-}KCl\text{-}TiCl_2$ molten-salt electrolyte.
9. Wet-chemical, spectrochemical, and fusion procedures have been developed and refined for accurately assaying common impurities such as chlorine, nitrogen, oxygen, hydrogen, iron, and magnesium in sponge metal and vanadium, iron, and silicon in $TiCl_4$. Procedures were developed for determining the average effective valence of titanium in molten salts. These procedures have played a significant role in the development of commercial and experimental titanium production processes.
10. Pioneering investigations have been made in virtually every aspect of titanium production, some of which are being continued in the private sector.

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