

# Entrepreneur India

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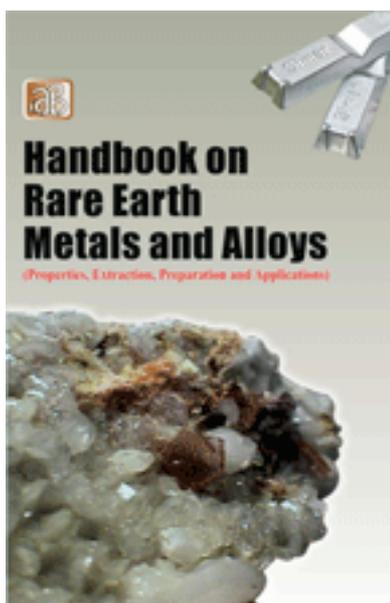
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Handbook on Rare Earth Metals and Alloys  
(Properties, Extraction, Preparation and Applications)



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Rare earths are essential constituents of more than 100 mineral species and present in many more through substitution. They have a marked geochemical affinity for calcium, titanium, niobium, zirconium, fluoride, phosphate and carbonate ions. Industrially important minerals, which are utilized at present for rare earths production, are essentially three, namely monazite, bastnasite and xenotime. In modern time techniques for exploration of rare earths and yttrium minerals include geologic identification of environments of deposition and surface as well as airborne reconnaissance with magnetometric and radiometric equipment. There are numerous applications of rare earths such as in glass making industry, cracking catalysts, electronic and optoelectronic devices, medical technology, nuclear technology, agriculture, plastic industry etc. Lot of metals and alloys called rare earth are lying in the earth which required to be processed. Some of the important elements extracted from rare earths are uranium, lithium, beryllium, selenium, platinum metals, tantalum, silicon, molybdenum, manganese, chromium, cadmium, titanium, tungsten, zirconium etc. There are different methods involved in production of metals and non metals from rare earths for example; separation, primary crushing, secondary crushing, wet grinding, dry grinding etc. The rare earths are silver, silverywhite, or gray metals; they have a high luster, but tarnish readily in air, have high electrical conductivity. The rare earths share many common properties this makes them difficult to separate or even distinguish from each other. There are very small differences in solubility and complex formation between the rare earths. The rare earth metals naturally occur together in minerals. Rare earths are found with non metals, usually in the 3+ oxidation state. At present all the rare earth resources in India are in the form of placer monazite deposits, which also carry other industrially important minerals like ilmenite, rutile, zircon, sillimanite and garnet.

Some of the fundamentals of the book are commercially important rare earth minerals, exploration for rare earth resources, rare earth resources of the world, some rare earth minerals and their approximate compositions, rare earths in cracking catalysts, rare earth based phosphors, interdependence of applications and production of rare earths, uranium alloys, conversion of ores to lithium chemicals, characterization and analysis of very pure silicon, derivation of molybdenum metal, electroplating and chromizing, electrolytic production of titanium, heat treatment of titanium alloys, tensile properties of alloys etc.

The book covers occurrence of rare earth, resources of the world, production of lithium metals, compounds derived from the metals, chemical properties of beryllium, uses of selenium, derivation of molybdenum metals, ore concentration and treatment and many more. This is a unique book of its kind, which will be a great asset for scientists, researchers, technocrats and entrepreneurs.

## **Content:**

Natural Abundance

Occurrence of Rare Earths

1. Placer Deposits
2. Vein Type Deposits
3. Bastnasite Deposits
4. Ion Adsorption Type Ores
5. Other Rare Earth Sources

Commercially important Rare Earth Minerals

1. Monazite
2. Bastnasite
3. Xenotime

Exploration for Rare Earth Resources

Rare Earth Resources of the world

1. China
2. United States of America
3. India

1. Beach Placers and Dunes

2. Inland Placers
3. Reserves of Monazite
4. Occurrence of Xenotime

4. Australia

1. Placer Deposits
  2. Hard rock Deposits
1. Mount Weld Deposit
  2. Mary Kathleen
  3. Port Pirie
  4. Olympic Dam
  5. Brazil

Other countries

Table 1.  
The Content of Rare Earths and Some Common Elements in the Igneous Rocks of the Earth's Crust

Table 2.  
Some Rare Earth Minerals and their Approximate Compositions

Table 3.  
Typical Placer Minerals and their Specific Gravity

Table 4.  
Mineralogical Composition of Typical Placer Samples, as mined in India and Australia

Table 5.  
Rare Earth Distribution in Various Rock Forming and Accessory Mineral of Host Rock

Table 6.  
The Rare Earth Pattern in Different Layers of an Ion Adsorption Type Deposit

Table 7.  
Composition of REO recovered from major Ion-Adsorption Type Deposits in China

Table 8.  
The REO Content of Different Types of Ores in China

Table 9.

Analysis of the Typical Loparite Sample

Table 10.

Rare Earths Distribution in Monazite from Different Sources (wt %)

Table 11.

Rare Earth Distribution in REO from Bastnasite from different Sources (wt. %)

Table 12.

Rare Earth Distribution in Xenotime Samples (wt.%)

Table 13.

Ore Types In Baiyunebo Deposit

Table 14.

Chemical Analysis of Ore Samples from Deposit no. 801, China

Table 15

Some Important Rare Earth Resources of Australia and their Rare Earth and Thorium content

Table 16

Countrywise Distribution of Rare Earth Resources

1. Arc Carbons

Glass Making Industry

1. Decolourization of glass

2. Colouring of glass

3. Special Glasses

1. Spectacle Glass

2. Television and Cathode Ray Tubes

3. Glass for Eye protection

4. Infrared Transmitting Glass

5. Radiation Protection Windows

6. Optical Glass

Laser Glass

Fibre

Glass Polishing Powders

1. Glass Polishing Technology

2. Different Types of Abrasives

3. Manufacturing Methods

4. Producers of Polishing Powders

4. Enamels and Glazes

Catalysts

1. Rare Earths in Cracking Catalysts .

1. Cracking Process

2. Evolution of the catalyst

3. Rare Earth, Exchange of the Zeolite

4. Composition of the catalyst

5. Role of Rare Earths in the Catalyst

Use of Rare Earth Zeolites

6. Rare Earth Consumption

7. Impact of Lead Additive Phase down

8. Scope for using cerium in FCC unit  
2. Application of Cerium and Lanthanum in Auto-exhaust Catalysts

1. Catalyst Converter System

2. Role of Rare Earths

3. Other Catalyst Applications of Rare Earths

1. Methanation

2. Ammonia Synthesis

3. Homogenous Catalysis

4. Methane Conversion

Fine Ceramics

1. High Temperature Structural Ceramics

1. Stabilization of Zirconia

2. Sintering of Silicon Nitride ( $\text{Si}_3\text{N}_4$ )

3. Sintering of Silicon Carbide ( $\text{SiC}$ )

2. Functional Ceramics

1. Piezoelectric Materials

1. Role of REO in Piezoelectric Ceramics

2. Applications of Piezoelectric Ceramics

2. Optoelectronic Materials

1. Applications

2. Preparation of PLZT Materials

3. Thermistor, Varistor and Capacitor Materials

1. PTC Thermistor

2. Varistor Materials

3. Grain Boundary Barrier Layer (GBBL) Capacitors

4. Solid Oxide Fuel Cells

1. Electrolyte

2. Electrodes

3. Interconnecting Material

5. Oxygen Sensors

6. Heating Elements

7. High Temperature Super-conducting Materials

Rare Earth Based Phosphors

1. General

1. Laser Action

2. Antistoke Emission

2. Rare Earths as Phosphor Materials

1. Fluorescence due to 4f Transitions

2. Fluorescence due to Transitions from 5d to 4f Orbital

3. Rare Earths as Phosphor Matrices

3. Major Applications of Rare Earth Phosphors

1. Low Pressure Mercury Lamps

1. Desirable Phosphor Properties for Fluorescent Tubes

2. Phosphors used in Tube Lights

3. Rare Earth Phosphors in Fluorescent Tubes

2. Rare Earths in High Pressure Mercury Vapour Lamps

### 3. Trichromatic Compact Lamps

#### 1. Matching of Lamp Light to the Visual System

#### 2. Red Phosphor

#### 3. Green Phosphor

#### 4. Blue Phosphor

#### 5. Performance of the Trichromatic Lamp

#### 4. R&D in phosphor Development in India

#### 5. Preparation of Light Phosphors

#### 6. Application of Cathodoluminescence of Rare Earth

#### 1. Colour Television Phosphors

#### 2. Preparation of Phosphors

#### 7. Phosphors for Non-illumination Purposes

#### 8. Electroluminescent Phosphors

#### 9. Thermoluminescent Phosphors

#### 10. Rare Earth X-ray phosphors

#### 1. X-ray screens and scanners

#### 2. Advantage of Rare Earth Phosphors

#### 3. Rare Earth Compounds used in X-ray phosphors

#### 11. Rare Earths in other Medical Imagery

#### Rare Earths in Nuclear Technology

#### 9. Miscellaneous Applications

#### 1. Application in Agriculture

#### 1. Techniques of Application

#### 2. Nong-le and N.P.K. Fertilizers

#### 3. Areas of Application

#### 2. Dyeing and Currying

#### 3. Colouring of Plastics

#### Interdependence of Applications and Production of Rare Earths

#### Introductory

#### Particle Characteristics

#### Middlings

#### Table 1.

#### Types of Middling

#### Staged Concentration

#### Panning

#### Gravity Separation

#### Chemical Methods

#### Flotation

#### Magnetic and Electric Methods

#### Amalgamation

#### Exploitable Factors

#### Concentration Formulae

#### Preliminary

#### Crushing

#### Crushing Theory

#### Physical Aspects of Comminution

The Crushing Sequence

Jaw Crushers

Variations on the Blake

The Dodge Crusher

Gyratory Crushers

Comparison of Jaw and Gyratory Crushers

Mobile Crushing Units

By-passing the Undersize

Feeding Arrangements

Protective Devices

The Duty of the Section

Lay-out and Equipment

The Symons Cone Crusher

Gearless Gyratories

ROLLS

Hammer Mills

Gravity Stamps

Dry Crushers, Summarised

Optimum Grind

Applied Power

“Useful” or Net Power

Grinding and the Particle

Grinding Objectives

Comminution of Particles

Effect of Peripheral Speed

The Return Load

The Solid-Liquid Ratio

Control

Preliminary

Fixed-path Mills

The Vibrating Mill

Tumbling Mills

Operation

Application

Mill Capacity

General Conclusions

Preliminary

Milling Action

Types of Mill

The Hardinge Mill

The Low-discharge Cylindrical Mill

Tube, or High-discharge Mills

The Cascade Mill

Mill Liners

Feeding

Crushing Bodies

Capacity  
Introduction  
Isotopes and Nuclear Reactions  
OCCURRENCE AND SOURCES  
PRODUCTION AND ECONOMIC STATISTICS  
CONCENTRATION FROM ORES  
REFINING  
PREPARATION OF METAL  
PHYSICAL PROPERTIES  
MECHANICAL AND METALLURGICAL BEHAVIOUR  
Hardness  
Elastic Properties  
Tensile Properties  
Creep  
Fatigue  
Deformation and Textures  
Recovery, Recrystallization, and Grain Growth  
RADIATION DAMAGE  
CHEMICAL BEHAVIOUR: REACTIONS AND COMPOUNDS  
Reactions with Nonmetallic Elements; Binary Compounds  
Reactions with Simple Compounds of Nonmetallic Elements  
Reactions with Aqueous Solutions  
Uranium Alloys  
Nonmetals: Carbon, Boron, and Silicon  
Metals  
Liquid Metals  
Phase Diagrams  
Table 13. Alloying Behavior of Uranium  
Metallography  
Melting and Casting  
Forging  
Rolling  
Extrusion  
Swaging and Drawing  
Machining  
Welding  
Powder Metallurgy  
USE OF URANIUM  
In Nuclear Reactors  
Other Uses  
INTRODUCTION  
OCCURRENCE  
Cost Considerations  
CONVERSION OF ORES TO LITHIUM CHEMICALS  
Production of Lithium Metal by Fused Salt Electrolysis  
PHYSICAL PROPERTIES AND HANDLING OF THE METAL

Lithium Cartridges

Lithium Wire or Ribbon

Lithium Shot

Sodium-Free Lithium Metal

Molten Lithium

COMPOUNDS DERIVED FROM THE METAL

Lithium and Hydrogen

Lithium and Nitrogen

Lithium and Oxygen

Lithium and Silicon

OTHER LITHIUM COMPOUNDS

Lithium Hydroxide

Lithium Halides

Various Other Lithium Compounds

ELECTROCHEMISTRY OF LITHIUM

Alloys

Lithium-Magnesium Alloys

Lithium-Aluminium Alloys

Lithium-Zinc Alloys

Lithium-Lead Alloys

USES OF LITHIUM METAL

Lithium in Alloys

Lithium as a Degasifier and Refining Agent

Lithium in Cast Iron

Lithium in Steels

Lithium in Organic Chemistry

Lithium in Atomic-Energy Developments

Lithium in High-Energy Fuels

USES OF LITHIUM COMPOUNDS

INTRODUCTION

OCCURRENCE

PRODUCTION AND ECONOMIC STATISTICS

DERIVATION

Copeaux-Kawecki Process

Sawyer-Kjellgren Process

PRODUCTION

Pure Beryllium Oxide

Beryllium Metal

Beryllium-Copper Master Alloy

PHYSICAL PROPERTIES

Beryllium

Beryllium Oxide

CHEMICAL PROPERTIES OF BERYLLIUM

TOXICITY

MECHANICAL PROPERTIES

Beryllium

Beryllium Alloys

FABRICATION

Beryllium

Beryllium-Copper Alloys

APPLICATIONS

Beryllium

Beryllium Oxide

Beryllium-Copper Alloys

Beryllium-Nickel Alloys

Beryllium-Iron Alloys

Miscellaneous Beryllium Alloys

INTRODUCTION

OCCURRENCE

DERIVATION

PHYSICAL PROPERTIES

The Solid State

The Liquid State

The Vapour State

Electrical Conductivity

Effect of Light on Electrical Properties of Selenium

CHEMICAL PROPERTIES

Oxygen

Hydrogen

Halogens

TOXICITY

USES OF SELENIUM

Electronics Industry

Glass and Ceramics Industry

Pigment Industry

Steel Industry

Miscellaneous Uses

INTRODUCTION

OCCURRENCE

PRODUCTION AND ECONOMIC STATISTICS

DERIVATION

Extraction of Platinum Metals from

Canadian Nickel Ores

Extraction of Platinum from South African Ores

Refining of Platinum Metal Concentrates

Treatment of Native Platinum

Refining of Scrap

FABRICATION TECHNIQUES

Melting

Working

Electrodeposition

Vapour Deposition

Available Forms

## PHYSICAL PROPERTIES

Platinum

Palladium

Rhodium and Iridium

Ruthenium and Osmium

Alloys of the Platinum Metals

## CHEMICAL PROPERTIES

Compact Metals

Sponge and Powdered Metals

“Blacks” and Colloidal Metals

## APPLICATIONS

Platinum

Palladium

Rhodium

Iridium

Osmium

Ruthenium

History

Occurrence and Sources

Production and Price Statistics

Extraction

Production of Tantalum Metal

Consolidation and Purification

Physical Properties

Mechanical Properties

Chemical Properties

Alloys

Tantalum-Tungsten Alloys

Fabrication

Applications

Surgical

Nuclear Energy Systems

Miscellaneous

## CALCIUM

Derivation

Physical Properties

Mechanical Properties

Applications

Calcium Hydride

Calcium Alloys

## BARIUM

## STRONTIUM

## INTRODUCTION

## OCCURRENCE

## PRODUCTION AND ECONOMIC STATISTICS

DERIVATION

PHYSICAL PROPERTIES

CHEMICAL PROPERTIES

APPLICATIONS

SINGLE CRYSTALS

CHARACTERIZATION AND ANALYSIS OF VERY PURE SILICON

INTRODUCTION

OCCURRENCE

PRODUCTION AND STATISTICS

Prices

ORE PROCESSING

DERIVATION OF MOLYBDENUM METAL

Powder Metallurgy Process

Arc-Casting Process

WORKING OF MOLYBDENUM

PHYSICAL PROPERTIES

MECHANICAL PROPERTIES

Corrosion Resistance of Metallic Molybdenum

PROTECTION FROM OXIDATION

MOLYBDENUM COMPOUNDS

FABRICATION

JOINING

APPLICATIONS

Molybdenum as an Alloying Element

OCCURRENCE

PRODUCTION AND ECONOMIC STATISTICS

DERIVATION

PHYSICAL PROPERTIES

CHEMICAL PROPERTIES

FABRICATION

ALLOYS

APPLICATIONS

OCCURRENCE AND CHARACTERISTICS

USES OF CHROMIUM ORE

CHROMIUM METAL

Alumino- and Silicothermic Chromium

Carbon-Reduced Chromium

Electrolytic Chromium

PHYSICAL PROPERTIES OF CHROMIUM

Electronic Structure

Thermal Properties

CHEMICAL PROPERTIES

ANALYSIS OF CHROMIUM

CHROMIUM TOXICOLOGY

MELTING AND FABRICATION

MECHANICAL PROPERTIES

TENSILE PROPERTIES

TRANSITION TEMPERATURE

Electroplating and Chromizing

CHROMIUM ALLOY SYSTEMS

APPLICATIONS

INTRODUCTION

OCCURRENCE

PRODUCTION AND STATISTICS

DERIVATION

Initial Recovery

Purification

Recovery

Purification

PHYSICAL PROPERTIES

CHEMICAL PROPERTIES

Toxicity

ALLOYS

Binary Systems

Ternary Systems

FABRICATION TECHNIQUES

APPLICATIONS

INTRODUCTION

OCCURRENCE

HISTORICAL REVIEW

PROCESSES FOR MAKING BORON

PRODUCTION OF BORON 10

PHYSICAL PROPERTIES

CHEMICAL PROPERTIES

METHODS OF ANALYSIS

FABRICATION TECHNIQUES

APPLICATIONS

OCCURRENCE

PRODUCTION

EXTRACTIVE METALLURGY

Oxide Reduction

Magnesium Reduction of Titanium Tetrachloride

Sodium Reduction Titanium Tetrachloride

The Iodide Process

Electrolytic Production of Titanium

PHYSICAL AND MECHANICAL PROPERTIES

CHEMICAL PROPERTIES

Corrosion

Oxidation

Chemical Compounds

PHYSICAL METALLURGY

Alloying Principles

Heat Treatment of Titanium Alloys

Metallography

PROCESSING AND FABRICATION

Melting

Fabrication

APPLICATIONS OF TITANIUM

INTRODUCTION

OCCURRENCE

PRODUCTION AND ECONOMIC STATISTICS

METALLURGY

Ferrotungsten

Tungsten Compounds

Tungsten Metal

Reduction

Tungsten Carbide

PHYSICAL PROPERTIES

MECHANICAL PROPERTIES

CHEMICAL PROPERTIES

ALLOYS

Tungsten-Molybdenum, Columbium, Tantalum, Chromium

Tungsten-Rhenium

Tungsten-Iron

Tungsten-Cobalt

Tungsten-Nickel

Tungsten-Nickel-Copper

Tungsten Steels

Miscellaneous

ANALYSIS AND METALLOGRAPHY

FABRICATION

Ductile Rod and Wire

Tungsten Sheet

Slip Casting

Arc Casting

Electron Beam Melting

Hydrostatic Compacting

Flame Spraying

Sintered Carbide

APPLICATIONS

Present Applications

Potential Applications

INTRODUCTION

Sources of zirconium

ORE CONCENTRATION AND TREATMENT

Separation of Zirconium and Hafnium

PRODUCTION OF DUCTILE ZIRCONIUM METAL

Reduction of  $ZrO_2$

Reduction of Zirconium Halides  
Reduction of Other Compounds  
Reduction of  $ZrCl_4$  with Mg—the Kroll Process  
Iodide Decomposition Process  
Electrodeposition of Zirconium  
Physical and mechanical properties

## CHEMICAL PROPERTIES

Reaction with Gases  
Reaction with Halogens  
Miscellaneous

## CORROSION RESISTANCE

Corrosion in Various Media  
Corrosion in Gases  
Corrosion in Liquid Metals  
Corrosion in Other Media

## MELTING ZIRCONIUM

## FABRICATION

Rolling and Forging  
Extrusion  
Cold Working  
Machining  
Power Brake Forming  
Surface Finishing  
Welding

## ZIRCONIUM-ALLOY SYSTEMS

Tensile Properties of Alloys  
Zircaloy

## APPLICATIONS

### **Sample Chapter:**

# RARE EARTH RESOURCES

The group of 15 chemically similar elements with atomic numbers 57 through 71 inclusive and yttrium (atomic number 39) are considered Rare Earths. Though two misconceptions concerning rare earths stem from the name itself such as they are rare and they are earths it needs to be stressed that both are only historical hangovers and they are in fact neither rare nor earths. This realization is essential to appreciate the role they play in modern life and technology and to not only explore but also to achieve new and rewarding applications for them.

## Natural Abundance

All the rare earths except promethium (Z 61) occur on the planet earth. The absence of promethium in terrestrial sources is due to its radioactive nature coupled with a short half life ( $t_{1/2}$ ) of only 2.7 years. Rare earths are widely dispersed in many minerals. For knowing the relative abundance of individual rare earths in the earth as a whole it is useful to consider the composition of a group of meteorites called carbonaceous chondrites. There are several geochemical evidences to show that the earth and these meteorites had a common origin. The data of Schmitt et al<sup>1</sup> on the rare earth content of these meteorites shown in Fig. 1 indicate that the abundance decreases with increasing atomic number and significantly a rare earth with even atomic number is more abundant than its odd atomic number neighbours. Elements are enriched or depleted in the igneous rocks relative to chondrites and for this a number of geochemical reasons have been advanced. The concentration of rare earths in the igneous rocks of the crust is much higher relative to that of the earth as a whole. The crustal abundance data for rare earths and for some common metals show that at least some of the former are no less abundant if not more abundant than some of the latter.

## Occurrence of Rare Earths

Rare earths are essential constituents of more than 100 mineral species and are present in many more through substitution. They have a marked geochemical affinity for calcium titanium niobium zirconium fluoride phosphate and carbonate ions. Based on chemical type nine groups of rare earth minerals can be distinguished. They are (1) fluorides (2) carbonates and fluoro carbonates (3) phosphates (4) silicates (5) oxides (6) arsenates (7) borates (8) sulphates and (9) vanadates. The first five of these are of significance for the recovery of rare earths industrially. Some typical examples of each of these types and their approximate chemical composition are shown in Table 2.

The similar atomic structure of rare earth elements is reflected not only in their chemical and physical properties but also in their close geochemical association in nature. The rare earth bearing minerals carry a suite of all the elements of this group. However the relative abundance of individual members is not the same in all minerals. There is a preferential enrichment of either the cerium group (light rare earths) or the yttrium group (heavy rare earths) among the minerals. Monazite bastnasite and other minerals bearing light rare earths are more abundant than minerals like xenotime which carry the heavier members of the family. Industrial production of rare earths at present is confined essentially to the three minerals monazite and bastnasite which are rich in light rare earths and xenotime which is rich in yttrium and heavy rare earths. The geological environments in which the rare earth minerals are found vary widely.

## Placer Deposits

Placer deposits are the major source of monazite and xenotime the two commercially important phosphate minerals. Placer minerals are formed by natural erosion and weathering of igneous and metamorphic rocks in which the two rare earth minerals along with ilmenite rutile zircon magnetite and a few others occur in small concentration. Natural agencies like water ice atmospheric gases and sun play an important role in these processes. Streams and rivers transport the weathered part of the rock and carry the released

mineral particles. During their transportation two forces act on the particulate matter (1) the current which carries them forward and (2) their own weight which pulls them down. The eddy currents lift some of the particles that settle and push them forward. While clay minerals get finer and finer as they travel down stream hard heavy and chemically resistant particles get abraded and become smooth and round. As the velocity of the current decreases some of the heavy minerals get concentrated in traps within the river system itself. These are the alluvial placers. Some of the heavy minerals reach the sea.

Though the mineral sands are expected to concentrate near and around the river mouths as the velocity of flow decreases considerably at that point the waves approaching the shore at an angle distribute them along the coast. Therefore placer deposits usually extend over several kilometers on either side from the mouth of the river. The breaking waves pick up all available loose sand of the near shore material and throw it on the beach. On the other hand the receding water which has lost most of its kinetic energy carries back to the sea preferentially the light material. If the process of sorting proceeds for a long enough time it leads to the formation of beach placers. The nature and richness of placer deposits depend as much on the conditions of the sea and the beach as that of the source rocks. Beach placers usually occur in the narrow strip between the high and low tide levels. Concentration of heavy minerals in the bottom layers of the sand in the shallow waters near the coast is also common. During the ice ages when the sea level was much lower than at present several rivers would have had to flow further than at present to meet the sea. Deposition of placer minerals would have taken place in their valleys but at present thick sediments have covered them. If they are not at too great a depth they can be mined from under the waters.

Some of the typical minerals which are associated with monazite and xenotime in the placer deposits are shown in Table 3.

Monazite and xenotime are usually minor constituents in the placers and they are recovered as byproducts but in the form of high grade concentrates while undertaking the commercial production of other heavy minerals like ilmenite rutile zircon and cassiterite.

Large beach coastal and inland placer deposits occur in many places spanning the continents of Africa Asia America and Australia. The important ones are the deposits in Australia India Brazil South Africa USA and China. Similar deposits which contain a combination of monazite and xenotime are found in the form of tin bearing alluvial placers in Malaysia and other south east Asian countries. In case of placer deposits nature has conveniently concentrated the heavy minerals thus eliminating the need for extensive drilling blasting and in some cases acid leaching. It can generally be said that placer resources of rare earths have more chance to come to fruition than their hard rock counterparts when discovered.

#### Vein Type Deposits

Stray occurrence of rich veins having a high content of monazite has been found in some parts of the world. One such deposit was discovered in 1950 at Steen Kampskrall in the Republic of South Africa. At that time it was considered to be the richest source of monazite. The other primary monazite deposits of commercial importance are located in Colorado (USA) and Baiyunebo (China).

#### Bastnasite Deposits

Bastnasite occurs in a finely divided form or as phenocryst in carbonatites. Quartz veins and epithermal fluorite bearing veins also contain this mineral. The first major discovery of a bastnasite deposit was at Mountain Pass in California in 1949. For quite some time after its discovery this was considered the world's largest rare earth deposit. Bastnasite occurs here in the carbonatite bodies intruding a Precambrian basement complex. The main orebody mined by MolyCorp is about 750 m long and up to 210 m wide. The ore contains 12% bastnasite 25% barytes 10% quartz 10% strontianite and 40% carbonates.

Rare earth bearing carbonatites are also located in some parts of Africa including Burundi Kenya and Malawi. Some of these also yield pyrochlore and monazite. A carbonatite complex located in the Minas Gerais region of Brazil can be a good source of niobium monazite and a few rare minerals.

A rare earth deposit of great importance and presently the world's largest one is in Baiyunebo Inner Mongolia China. Here bastnasite and monazite occur together as associated minerals in a major iron ore deposit. Somewhat similar deposits are also identified in South West and South East parts of that country.

#### Ion Adsorption Type Ores

The ion adsorption type deposits are weathered residues where rare earths are adsorbed on clay type minerals. Commercially attractive quantities of this ore type have been found so far only in parts of China and they play a very significant role in the development of rare earth industry of that country. They have already attracted the interest of other countries as a source material. This material has some desirable characteristics which no other type of ore possesses.

The ion adsorption deposits are the result of in situ weathering of rare earth rich host rocks most commonly granitic and volcanic types. There are two important prerequisites for the formation of these deposits. First there must be a sufficiently large body of rare earth bearing host rock occurring within the zone of weathering and second the weathering or lateritic process must be for a prolonged period with limited erosion. This requires a mild rainy and tectonically stable environment over a geologically long period of time. In Southern China where both conditions are met a large number of deposits of this type have been found. The granitic rocks of Yinshen age (195-130 million years old) are the most common host rocks for such deposits. Bastnasite, synchisite, allanite and perrierite are the rare earth bearing minerals present in the weathered zone of these ion adsorption deposits. The stability of the rock forming minerals and accessory minerals like plagioclase, biotite, manganese garnet, titanite and epidote to the chemical weathering process is also a critical factor in the formation of these deposits. In many formations of this type the rare earths are distributed in both the rock forming and accessory minerals of the weathering host rocks.

Weathering is the most important factor in the formation of ion adsorption deposits in which several horizons can be distinguished such as (i) an upper horizon of colluvium and soil underlain by (ii) a thick zone of strongly weathered rock enriched in rare earth elements (iii) a less weathered transitional zone over (iv) a basal hard rock.

One important feature which distinguishes the ion adsorption ores of China from any other ore in the world is the depletion of cerium particularly in the strongly weathered zone of the deposits. Consequently there is lanthanum enrichment in these materials. The highly oxidizing conditions prevalent in the upper leach regions of the deposit result in oxidation of  $Ce^{3+}$  to  $Ce^{4+}$  leading to its hydrolysis and retention by the top soil layers. Middle rare earths like samarium and heavies are more abundant in the material from deeply weathered zones.

The characteristics of the ion adsorption type ores which make them attractive for rare earth producers are (i) low cerium content (ii) relatively high yttrium content in some and middle rare earths content in others and (iii) easy mining and processing to recover rare earths. Table 7. shows the varying composition of the rare earth oxide product recovered from different ores of this type originating from different mines in China. The actual rare earth content of the ion adsorption type of ores is much less than that of other types of ores. However a major advantage with these ores is their amenability to a simple chemical leaching which leads to a high grade rare earth oxide product with very few processing steps.

The highly variable rare earth composition of the ion adsorption ores with respect to combined lanthanum and cerium content as well as other rare earths content makes these ores very attractive for selective mining to meet the required production targets of individual rare earths. This aspect more than the total rare earth reserves in this form plays an important role in China's strategy for producing individual rare earths.

#### Other Rare Earth Sources

In addition to the types of deposits mentioned there are others in some countries which play a role in

providing rare earths in significant quantities.

# NON METALLIC APPLICATIONS OF RARE EARTHS

Early applications of rare earths on an industrial scale started with the use of their compounds particularly the oxides and fluorides. Use of cerium in the Welsbach gas mantle though as a minor addition to thorium nitrate falls in line with this trend. This was followed by their use in several fields and it is surprising that some of these applications continue to the present time. Some of the important areas where compounds of rare earths are used industrially in varying degrees of purity are outlined here.

## Arc Carbons

Soon after Welsbach commercialized gas mantle production mixed rare earths started accumulating at all the monazite processing plants. Production of mischmetal for lighter flints provided an outlet for this byproduct. Another application was developed by Electrodes Bergenlicht Co. of Germany by way of manufacture of arc carbons during World War I. This was essentially a military application for search lights and was based on the observation that in a carbon arc the rare earths emit a bright light. Initially attempts were made to incorporate rare earths in the carbon electrodes in different ways. One such way was to soak the rods in a solution of mixed rare earths but the effect was not good. After several modifications it was finally found that incorporating the rare earth compounds in the core of one of the electrodes used for striking the arc brought about the expected result. In the early version of such an electrode a thin metal wire was incorporated in the rare earth mixture to make it a good conductor. The process of electrode preparation underwent a change later.

It is interesting to note that in Japan the industrial processing of rare earths began with the manufacture of rare earth fluoride during World War II for military applications such as fabrication of powerful searchlights. Today Japan stands as one of the major users of rare earths for the very mundane to the most sophisticated applications and has a variety of production facilities for rare earth products.

Radiant arc is the light source for search lights and in the civilian field for motion picture projectors. Radiation of reasonable brightness is produced by an arc struck between two carbon electrodes. In a steady arc the prevailing high temperature vapourises and ionizes the carbon. However the light from a carbon arc is basically of the low intensity type. When the era of colour motion pictures came into being it was realized that the simple carbon arc was not bright enough to project these pictures on a wide screen. The need for development of a much brighter source of light with good spectral quality arose. It was in this context that cored carbon electrodes were developed.

Compounds of rare earths usually mixed rare earth oxide and fluoride with minor addition of other metal salts are kneaded with pitch and packed as core in the positive carbon electrode. The shell of the electrode is the main conductor. As the arc is struck between the electrodes the core vapourises faster than the shell (made of carbon) thus forming a cup on the face of the positive carbon which is the main source of light. The rare earth compounds vapourise from the cup shaped crater and emit brilliant light as they provide abundance of spectral lines favourable energy distribution high light intensity and good colour balance. The use of mixed rare earths is essential for getting balanced light.

It is reported that due to difference in composition of rare earths the mixed rare earths product derived from bastnasite is not so good for this application as the one derived from monazite. Considerable quantity of mixed rare earth compounds is utilized for this purpose in the world. Up to 1960s nearly one fourth of the rare earths produced in the world were used in this field. However with the emergence of halogen lamp as radiant source the demand for arc carbons has diminished to some extent.

## Glass Making Industry

The applications of rare earths in the glass industry were among the very early ones to come into practice. Like in other fields in which rare earths are used the scope of application is modified and expanded over the years. Starting with the use of naturally occurring mixtures there has been a gradual sophistication in use needing moderate to high purity starting materials. The field of application can be conveniently split into several sectors (1) decolourization of glass (2) colouring of glass (3) making of special glasses and (4) glass polishing.

### Decolourization of glass

In the production of transparent glass presence of traces of divalent iron in the raw material is considered harmful as it imparts a bluish green colour to the manufactured glass. Oxidizing agents like manganese dioxide ( $MnO_2$ ) and arsenous oxide ( $As_2O_3$ ) were used for a long time to reduce or eliminate such colour. In 1896 Dressbak patented and manufactured a mixture containing cerium and other rare earth oxides for decolourizing glass. This was perhaps the first large scale use of cerium. The beneficial effect of cerium is attributed to  $Ce^{4+}$  which being a strong oxidizing agent converts  $Fe^{2+}$  in the glass melt to  $Fe^{3+}$  leaving only a faint yellow colour in the glass. The colour of the small amount of neodymium and praseodymium in the added rare earth mixture masks the residual yellow colour and makes the glass look colourless and transparent.

For the refining of glass by elimination of bubbles cerium oxide is as good as other additives like arsenous oxide. However the latter is a health hazard on account of its poisonous and carcinogenic nature.

When cerium is used to decolourize flint glass containers it absorbs ultraviolet light and thereby reduces the deterioration of ultra violet light sensitive materials like food chemicals or medicines stored in such containers.

### Colouring of glass

Rare earths are also well known as excellent colourants of glass. They can be used to manufacture both normal coloured glass and coloured optical glass.

Addition of 3.5%  $CeO_2$  to glass imparts beautiful yellow colour mixed with some light red. Addition of a mixture of  $CeO_2$  and titanium dioxide ( $TiO_2$ ) imparts to glass a bright golden yellow appearance.

Neodymium glass exhibits a beautiful wine red colour with soft tone and a remarkable double colour effect. Addition of  $Nd_2O_3$  along with manganous oxide and selenium makes the glass take a lilac colour. Different colours show up in different lights.

Glass with praseodymium addition shows green colour in the sun and nearly colourless in candle light.

Holmium and erbium impart light shades of colour but they are relatively costly for general use.

Rare earth colourants have been widely used in glassware production in China to make ornaments with beautiful bright colours<sup>2</sup>. The jewelry glass artificial crystals diamond pearl and agate made with rare earths have nearly 30 colours and tones. The application of rare earths in this field has good prospects.

### Special Glasses

Apart from colouring and decolourizing of common forms of glass some of the rare earths proved useful for manufacture of glass for special purposes.

#### Spectacle Glass

In 1912 Crooks found that addition of cerium to ophthalmic glass makes the latter absorb ultraviolet light a feature useful for eye protection. For this purpose high purity (+99.95%) cerium is used. For absorbing effectively all radiation below  $3200\text{\AA}$  both  $CeO_2$  and  $TiO_2$  are added to glass. Praseodymium and neodymium are added as didymium oxide for colouring Crooks glass.

#### Television and Cathode Ray Tubes

The filter glass used in colour television sets contains neodymium. This helps in filtering of all colours

except the three primary ones blue green and red rendering the screen bright and showing up a good contrast of colours.

Cerium is effective as a stabilizer to counteract browning of glass by cathode rays. Hence cerium oxide of 90% purity ( $\text{CeO}_2/\text{REO}$ ) is added to TV and cathode ray tube face plates. Since 1980 addition of neodymium (95-98% pure) to television tubes is practiced to cut off ultraviolet light. Consumption of cerium in the manufacture of television and cathode ray tubes is considerable. In Japan alone it is reported to be about 500t per year.

#### Glass for Eye protection

Glass with 2-4%  $\text{CeO}_2$  and small amount (0.5%) of praseodymium and neodymium added as didymium oxide absorbs both ultraviolet and infrared radiation. Such glass has long been used in the fabrication of glass blowers and welders goggles. It also effectively absorbs the yellow of sodium light

#### Infrared Transmitting Glass

Addition of some heavy rare earths to special glass confers on it wider transmission range of infrared. At the same time such addition brings about higher chemical stability for the glass. Glasses made with mixed fluoride additives like  $\text{ZrF}_4$   $\text{LaF}_3$   $\text{BaF}_2$  and  $\text{ZrF}_4$   $\text{ThF}_4$   $\text{LaF}_3$  and germanate glass with addition of zirconium oxide and lanthanum oxide has excellent infrared transmittance capacity.

#### Radiation Protection Windows

A specialized though not a bulk use of rare earths is the fabrication of thick lead glass slabs for radiation shields and windows in nuclear installations. On exposure to a high dose of radiation such lead glass normally develops colour centers and gets discoloured. Addition of about 3%  $\text{CeO}_2$  prevents this type of damage and maintains transparency over long periods. Since such windows are very thick even a small amount of praseodymium and/or neodymium results in severe lowering of the transmittancy of the glass. Hence for this purpose  $\text{CeO}_2$  of 99.9+% purity is required.

#### Optical Glass

From the beginning of the twentieth century efforts are on to make high dispersion glass with low refraction and low dispersion glass with high refraction for optical lenses. Schott Co. of Germany developed optical glass with high barium content to become the leader in the camera world before the wars.

After the war Eastman Kodak Co. of U.S. introduced special optical glass containing low silica and having lanthanum oxide as a component. Lanthanum incorporation in glass reduces dispersion by raising the refractive index. It also confers a high degree of chemical stability to the otherwise weak borate glass with respect to the action of water and acid at the same time increasing its hardness. Prior to the introduction of lanthanum glass it was necessary for fabricators of optical instruments like cameras microscopes binoculars etc. to combine several concave and convex lenses made of glass of different refractive indices and dispersion power for eliminating spherical and chromatic aberration of the image. Various borate glass systems containing oxides of rare earths and of some rare elements like niobium and tantalum provide lenses with large aperture wide field of view as well as long and variable focus.

## Methods of Separation

### Introductory

Economically there is a limit to the amount which can prudently be spent in grinding. Technically there are degrees of liberation which directly affect the efficiency of separation and the purity of the resultant products. The word *concentration* denotes the selective separation of the head feed into characteristic products. In the simple case of an ore containing galena ( $\text{PbS}$ ) and calcite ( $\text{CaCO}_3$ ) comminution followed by concentration might produce three fractions.

Here a concentrating process has been applied which has segregated the broken ore into three products

two of which are finished the valuable galena and the valueless calcite and one in which the two constituents remain interlocked as particles of *middlings*. Processing methods are normally concerned with physical separation only so nothing more need be done to products (1) and (3). If further treatment is decided on product (2) can be crushed finer and given another separating treatment.

This intermediate middling being composed partly of the sought concentrate galena and partly of the waste product calcite should neither be accepted as a concentrate nor rejected as a tailing. If accepted it would lower the grade and thus prejudice sales. If rejected its galena would be lost. In all concentrating processes the decision as to further treatment of middlings includes technical and economic considerations specific to the ore.

When the ore body contains more than one economically recoverable mineral treatment is more complicated. Not only does each species contribute a middling product but these middlings may contain more than one valuable mineral and thus lead to contamination of concentrate A by A B type middlings. Treatment must sometimes be elaborated in order to reach a specified degree of purity in the end product. In general terms a multi product flow sheet provides for series concentration as at Rammelsberg where *differential flotation* is used to produce a series of high grade concentrates serially.

#### Particle Characteristics

If comminution of the ore is efficiently performed each of the multitude of resulting particles acquires distinguishing characteristics which can be exploited by a suitable separating (concentrating) process. The treatment chosen in the case of the mixture of galena and calcite is applied to the pulp to make as complete a separation between the two minerals as their degree of liberation allows. It is not necessarily completed in a single step because of the presence of incompletely liberated middlings.

These (d) products could be disposed of as a low grade concentrate and a rich tailing re treated or stockpiled if better treatment facilities or higher realisation prices were expected in due course.

The characteristics of the particle undergoing treatment may combine to make the work of separation easy or they may interfere with each other making concentration difficult. To be usable they must be such that at the same time and in the same pulp the two kinds of particles (concentrate and tailing) do not to any important extent respond in the same manner to the chosen treatment.

#### Middlings

Provision is usually made in concentrating appliances for the separation of the feed into three products (a) *concentrate* (b) *middlings* and (c) gangue or *tailing*. In gravity separation a particle sufficiently coarse to move principally in accordance with its gravitational pull can be moved in one direction if clean and heavy and another if clean and light. If it consists partly of heavy mineral and partly of light gangue it either remains neutral or moves feebly in the direction either of the light or the heavy particles. This depends on which of its two component minerals predominates in the locked (incompletely liberated) middling. If the separating appliance has three exit channels this indeterminate middling forms a dividing band between the two finished products (concentrate and tailing) as shown in Fig. 1.

If the middling instead of being run through the appliance in open circuit is returned and mixed with new feed the total quantity of middling in the circuit increases until the position shown in Fig. 4 is reached. It is thus possible to give these hesitant particles more chances to sort themselves out. If they are made to issue from the appliance in a band lying between concentrate and tailing the separation is at the same time made more effective.

A 100% circulating load has been built up at the moment illustrated. For each eight units of new feed eight are being recirculated *via* the middlings band while eight leave the system three as finished concentrate and five as finished tailings.

While this happens new feed comes to the separating appliance and the middlings leaving is therefore increased beyond the 100% circulating load. This cannot continue indefinitely. A balance must be struck

between the amount returned and the amount of new feed. When the operation has steadied to this state of balance the position is again as depicted in Fig.1 save that the return circuit of middlings now provides an excellent dividing zone between concentrate and tail. As the separating appliance does not alter the degree of liberation of the middlings something more must be

If the separating appliance is unsuitable for the treatment of the ground middling the latter is sent to a more appropriate machine. Three important points in mill practice should now be apparent. First it is not necessary to begin by grinding *all* the minerals to their fully liberated state in order to procure clean separation. Results can frequently be achieved in stages. First comes grinding next separation into clean concentrate clean tailing and locked middling (as incompletely liberated particles are called). Finally the middling is unlocked by grinding and retreated.

*Second* the middling or any fraction of it can be held in a closed circuit if by doing so the work of separation is made more efficient.

*Third* a true middling always needs special treatment not provided for in the appliance which has sent it out as a middling. After this special treatment it may be unsuitable for return to the sorting appliance. In the case just considered if treatment depended on the mass of the particle the ground fragments should probably be sent to a machine specially adapted to deal with their smaller size.

### Types of Middling

Table 1. lists a number of mineral characteristics of which advantage may be taken to achieve separation. The behaviour of a middling can sometimes be strongly influenced by the characteristics of one of its minerals while the other part of the binary system offers little or no opposition. The coarser the grinding the cheaper it is and the greater the amount of middling made. Where binary particles are sufficiently responsive advantage can be taken of their breaking behaviour to cheapen the working costs without losing valuable mineral. Middling particles can be associated in various ways.

A particle of type (a) would need breaking before it could be correctly graded. Since half of its surface is gangue and half value it will respond well to surface attack such as is employed in chemical or flotation treatment Particle (c). in which the value is deposited as a shell on a core of gangue is likely to behave as a tailing in gravity work and as a clean concentrate in flotation (d) is usually lost in flotation but satisfactorily relieved of its value in a solvating process (a) (c). and (d). if the value is ferromagnetic should respond to electromagnetic pull. Particles (b) (c). (f). and (g) might act as gravity middlings. When the values are almost or quite masked by gangue they will be completely lost in flotation or chemical attack. Particle (g) can be a special case. Suppose the gangue to be quartz the outer enclosed mineral pyrite and the centrally enclosed mineral gold (the last being the value sought) then the grinding treatment must expose the gold. Regrinding must therefore be far more elaborate than in usual cases particularly if the gold is segregated in the pyrite in specks only a few microns in size. Here roasting treatment is usually preferred to further comminution.

Coarsely mineralised ores suitable for such treatment are now rare. Further most minerals can be cheaply concentrated at a fine m.o.g. by flotation so the need to avoid line grinding which dictated gravity concentration methods before 1920 no longer exists. If flotation is used as it is today in most mineral dressing plants instead of removing finished concentrates by stages it may be feasible to discard liberated gangue at each grinding stage as in Fig. 8.

This principle may be used to give selective treatment to the middlings product at each grinding stage as in Fig. 9.

This arrangement is a variation of the cascade principle which is used in chemical engineering to enrich or deplete an original feed by gentle stages.

The extent to which this principle of gentle upgrading is used in a given case depends on the operating difficulties which must be overcome and on the cost warranted by extra treatment.

## Panning

At this stage the student is recommended to practise separation of a heavy mineral from a light one by panning. This will familiarize him with the packing of sands the transporting power of a slurry the difference in behaviour of value middling and tailing particles and the difficulties encountered in attempting to treat a long ranged feed in a single operation. A clean prospecting pan should be used. Scouring with sand usually suffices to remove old rust. The pan should not contain oil or grease. If a gold ore is to be tested the pan should be dark in colour so as to show up the golden specks clearly. Since a great deal of panning is done in pools and streams the beginner should learn to squat on his heels and pan from one gold pan into another full of water so that he can save and retreat the discarded material until he has become expert.

An excellent practice material is a 20-mesh mixture of sand and galena. A few hundred grams of this material are wetted down into water and worked into a running pulp. This is next deslimed by gentle decantation the pan being held with its double riffle away from the operator. At no time should pulp be allowed to stream over the riffle. It should be floated out into the pool of water with a gentle swirling or rocking motion.

From time to time the pan should be tapped with the heel of the hand to aid the heavy particles to burrow down to the bottom of the fluid body of pulp. The top strata should then be panned off using a jiggling or swirling motion. As soon as heavy particles show the material still in the pan should be repulped and rethumped. Successive barren strata can thus be removed without loss of values. When the point is reached where most of the sand has been rejected the decision must be made as to whether a low grade concentrate and a clean tailing is to be produced or a high grade concentrate and a middling. In the latter case rejected sands which now carry heavy mineral should be panned out into another holding vessel. It is not possible to make a clean concentrate and a clean tailing in one operation. The rejected tailings should be repanned to see how efficiently the work was carried out. With practice it is possible to use panning as a rough guide in assessing efficiency of gravity treatment of sands.

The plaque a white enamelled concave disc 11 in diameter is used in a similar manner in the examination of fine sands.

## Gravity Separation

In gravity separation the combined effect of mass and shape of the particle determines its movement relative to flowing water. In one development of this effect the water flows vertically either continuously (classification) or in oscillating motion (jiggling). In a second method the ore is fed into a fairly quiet pool of dense media (water mixed with slow settling heavy minerals to form a fluid which can be maintained at a high specific gravity). Ore entering this dense medium either floats or sinks. A third type of gravity treatment uses flowing streams to effect separation. Here the pulp is carried horizontally) or down a slope and separation depends on the rate of fall and resistance to displacement after the particle reaches the floor of the appliance.

Methods which exploit differences of gravity require that there shall be a marked difference between the specific gravities of the value and the gangue. The material must be sufficiently coarse to move in accordance with Newton's law. Particles so small as to settle in accordance with Stokes' law are unsuitable for concentration by simple gravity methods. If centrifugal force is applied such fine particles can sometimes be treated. Gravity methods of separation become cumbersome and inefficient when the average particle is so minute that its surface friction dominates its movement through the surrounding fluid. Exploitation of differences between the specific gravities of particles below 150 to 200 mesh is difficult and usually avoided when alternative methods of treatment are available.

# PRIMARY CRUSHING

# Preliminary

Crushing grinding and other words or phrases associated with the size reduction of ore and other rock are all comprehended in the word comminution. This (Truscott) is the whole operation of reducing the crude ore to the fineness necessary for mechanical separation or for metallurgical treatment. It is usual to make an arbitrary division of comminution into convenient stages. Primary crushing brings run of mine ore down to a maximum size of the order 4 to 6 in average diameter secondary crushing receives feed at 6 and reduces it to below 3/4 . Dry crushing includes work on ore as mined which may be somewhat moist when delivered. It is succeeded by comminution in water arbitrarily called grinding . Although a considerable amount of fine grinding is done by dry methods this book follows usage by reserving the word crushing for an operation predominantly dry and grinding for work on a suspension of ore particles in water. One important difference between dry and wet comminution lies in the mode of seizure of the particle. In the former case the particle is large enough to be gripped between two solid steel members as they are pressed together by mechanical forces. One or both of these members moves to and from in a fixed path cycle. The rock gravitating through the rapidly expanding and contracting gap thus produced is nipped and crushed. In wet grinding the bulk of the ore is already too finely divided for a particle to be seized in this manner. It is therefore exposed while more or less free to move to random blows. There are exceptions to this generalisation.

Machines used in dry crushing must work in dusty conditions even when the main cause (escape of fine particles at transfer points) is dealt with. They are usually worked intermittently to fit in with the hoisting and delivery programme of the mine. On completion of the dry crushing their product is delivered to bulk storage (in the mill s fine ore bins). From these it is delivered at a controlled rate to the more continuous grinding and concentrating processes.

The nett energy consumed during equal reduction ratios in comminution increases with increased fineness of the ore being treated. From experimental evidence Hukki suggests an apportionment of this power consumption of 0.35 kWh/ton in primary crushing of a brittle solid rising to 0.6 in the secondary crushing 1.6 in coarse grinding and 10 kW/h in fine grinding in the ratios stated above. These in his view suggest an important change in the use made of the applied power through these stages. At the primary crushing level the results correspond statistically with the requirements of Kick s Law This phase is followed by approximate agreement with Rittinger s Law in the intermediate stage while Bond s formulation becomes increasingly good at the finer end of comminution. These laws are discussed below. The enormous rise in power consumption when a product well below a micron ( $\mu$ ) in size is aimed at more or less rules out the use of standard grinding techniques on the score of cost.

## Crushing

The main purposes are

Convenience in transport

Production for use without further treatment beyond screening of graded sizes and shapes

*Liberation* of specific mineral/s as a step in separate recovery from the ore

Exposure of contained values to chemical attack

Production of granular material suitable for treatment by gravity methods

Development of particles suitable for feed to froth flotation

The methods of treatment are discussed later in this book but must be recognised from the start as depending for efficiency on correct comminution. The proposed end use should dictate the stages and methods employed. A granite or limestone ballast for railroad beds or roadmaking would have no problem of specific liberation but would be concerned with particle shapes and sizes as these affected packing drainage through voids and structural strength. Preparation for the processing of an ore would call for

much finer crushing and grinding in which the cost which rises sharply when fine sands must be prepared as feed to the concentrating plant would be an important factor.

The earliest stage of rock breaking is in connection with the severance of the ore from its lode. This is performed by the use of suitable explosives applied in such a manner as to produce lumps of rock of a size convenient for handling in the mine's transport system. The interest of the alert ore dresser can well commence at this early point since the manner in which the abrupt stresses of explosion are applied to the rock *in situ* is one determinant of its *size range* crushability and total surface per unit volume from that point on to the next crushing stage. The lavish use of high explosive underground is to be depreciated first on grounds of cost second because the finely shattered ore thus produced is difficult to gather and transport and third because the delicate reactions used in treatment are jeopardised by random exposure of small particles between slope and process control in the mill.

Ore as broken may range in size from lumps weighing several tons down-ward but delivery passages chutes gates trucks and skips work best when they are not exposed to the shock loading of large pieces of dropped material and pack best when the sizes transported are reasonably *close ranged*. Severance may be followed by the use of explosive on large pieces of ore lying in the slope by sledging breaking down lump ore on a grating protecting an ore chute underground or at an underground crushing station where a jaw crusher of the Blake type is frequently installed. This machine should be set in the updraft ventilating zone so that the dust produced in crushing does not contaminate the mine air. Broken mine timber coming to the crusher with the ore must be removed. At all stages of ore treatment it is good practice to remove *trump iron* and other mining detritus as early as possible. The feed to the underground crusher must be adequately displayed and illuminated to facilitate hand picking by the crusher attendant.

Big tonnages of rock are crushed for use as graded sizes of stone or homo-geneous rock for road metal ballasting etc. Such dressing has nothing to do with mineral processing in which crushing is a stage in the liberation of values. Washing and sorting may be applied to the ore in transit and simple concentrating treatments may be used at the same time but the main purpose in crushing is to reduce the size of the rock particles by suitable stages so that the most efficient use of force is made and unnecessary comminution is avoided. For some purposes dry crushing must be used throughout the work e.g. in the grinding of cement dressing of mica talc and some other minerals. Generally comminution commences by dry crushing the ore to below a size established by tests and finishes by wet grinding to the required liberation size or *mesh of grind* (m.o.g.). The changeover from dry crushing to wet grinding lies between 3/4 and 1/4 and tends toward still lower sizes with the introduction of tougher alloys improvement in design and better methods of lubrication. These have led to the development of crushing machinery which can withstand the severe working stresses involved when large tonnages are crushed to gravel size.

### Crushing Theory

The forces used to produce fracture of a perfect crystal are of two main types. The structure is bound together by its inter atomic forces of attraction. Stress as considerable as 10 p.s.i. (pounds per square inch) is required to disrupt this bonding or theoretical strength which can be calculated. If tension is applied the crystal stretches elastically until it reaches its yield point and recovers if the stress is removed before this point is reached. Once the elastic limit is exceeded a flaw is produced usually in the form of a minute crack which becomes a focus for incipient fracture. In his classic paper Griffiths noted that the stress which the crystal can thenceforward withstand is inversely proportional to the square root of the length of the crack. This means that it will now fracture at a much diminished stress loading. During the stressing which created the imperfection work was done to overcome the mutual bonding of the inter atomic forces. This work was stored as elastic energy and was released as the atoms returned to their normal positions. Since a crack existed the atoms in its vicinity were able to shed elastic energy while the crystal was being stressed. If this released energy was sufficient to overcome the weakened inter atomic

bonds at the tips of the crack it grew rapidly (at a speed of about 15 000 ft/sec). The fact that stress of the atomic bonding is focused at crack tips has been proved by polarised light studies of plastic materials. Such a crack in solid material may start as a scratch or a surface blemish (a superficial discontinuity) as a minute fissure in a crystallite structure or as a defect in the atomic lattice of a crystal grain which by yielding permits the start of plastic flow. Most rocks and man made materials contain such foci of weakness so that practical strength falls far short of theoretical. Ideal glass should withstand stresses up to 10 p.s.i. but in practice failure occurs at about one ton p.s.i.

Where dislocations exist crystals which would otherwise deform plastically as one plane slides freely over another have this plasticity blocked at each such dislocation. Stress builds up at this point and the surrounding atomic bonds are ruptured. The result is a minute crack which given a little relatively light further stressing becomes a complete fracture. Once crack propagation begins it proceeds at nearly the speed of sound. A corollary is that once a crack is running at this speed no further stress applied to the main structure can catch up with the advancing fracture.

It is thus clear that two kinds of stress can operate the reversible which is removed if the crystal is not loaded to its elastic limit and the irreversible in which surface discontinuities are formed or plastic deformation occurs. This last is the result of the slipping of one plane of atoms over another. The slip is local and so produces a deformed area with one side in compression and the other in tension. Energy is thus stored ready for use in further deformation. Similar storage builds up in zones surrounding dislocations which prevent the free sliding of one atomic plane over another. Naturally occurring rocks contain random focal points where stresses due to defects are stored till an initial crack is produced by a relatively small further stress. Further weakening factors are the explosive shock during blasting of ore and its chemical oxidation between severance and milling.

In a piece of ore at least two mineral species are inter crystallised in various patterns. The situation is far more irregular than that in the perfect and completely pure crystal with which this discussion commenced. The practical application of crushing theory must therefore add statistical methods of testing and an empirical approach to the considerations outlined above. No two lumps of ore are precisely similar. It is common to think in terms of such varieties of disruptive force as compression tension shear torsion abrasion and shatter. The last four are compound forms of the first two. When a beam suspended at its ends is centrally loaded till it bends the lower part is in tension while the upper part is in compression. When seizure of a piece of rock occurs in such manner that the seizing forces move in opposing directions while the rock is prevented from rolling tensile shear predominates with local compression where its high points are gripped. Most crushing force is applied compressively. A piece of rock can be thought of as either a column or a beam loaded beyond bursting point. A piece of ore sufficiently large to be gripped forms a short pillar between approaching faces and is loaded to failure. If the ore bridges the crusher faces beam loading results. With the exception of the dynamic class of crushing device in which the particle becomes a projectile in a fast moving gaseous stream and acquires sufficient velocity to cause it to shatter itself on an impact plate (special cases which will not receive further attention in this book) application of stress by the crushing device is very slow in relation to the rate of propagation of a running crack. This is true even for such impact crushers as stamps and hammer mills.

Many attempts have been made to establish crushing principles on an un-assailable basis of fundamental law. Kick's law which Gaudin rightly says should have been regarded as a postulate states that the energy required for producing analogous changes of configuration in geometrically similar bodies of equal technological state varies as the volumes or weights of these bodies (Stadler). The Rittinger law which should be regarded also as a hypothesis states that the energy necessary for reduction of particle size is directly proportional to the increase of surface. If the sole force operating to produce crushing was used to disrupt molecular bonds along planes and thus to produce completely severed new particles Rittinger's

law would be in line with current physical concepts but this is an over simplification.

Something of the difficulty facing the research worker in the field of comminution may be appreciated when it is recalled that four types of binding force are recognised in fundamental physics. Taking nuclear force (that binding a proton to a neutron) as unity then electrostatic force (proton to electron) is  $10^{-10}$  nucleon decay force (emission of particle)  $10^{-10}$  and gravitational attraction indefinitely weak. Nothing is at present known of the balance between these forces which must be upset for cleavage to occur. Crystal study shows for a homogeneous material three types of imperfection which affect resistance to shear. Micro defects are lattice imperfections due to irregular ion distribution. They probably have a sub threshold effect on comminution though as will be seen when the physical chemistry of mineral surfaces is studied they modify flotation reaction. Macro defects are incipient strain areas flaws or discontinuities in an otherwise regularly repeated lattice structure which in the perfect crystal would be an orderly multiplication of its unit cell. Mosaic defects are typical in crystals in which orderly blocks (type 2) are constituents of the overall imperfect particle. Fortunately for the mineral engineer these considerations are of less importance than the empirical approach.

Basic research on the crushing characteristics of multi phased rock such as a piece of ore is hampered by the fact that no two pieces are alike. Repetition tests cannot therefore offer reliable evidence. Since comminution is the most expensive part of treatment and also exerts a critical influence on both concentration procedure and percentage recovery of values empirical test procedures have been developed for use in each specific problem and for each specific ore body. The main practical interest in a given case centres on two factors. The first is the manner in which the association of different mineral particles in a piece of rock can best be disrupted. The second is the effect on subsequent treatment of any new development in grinding methods.

A new approach to the theoretical consideration of crushing has been made by F. C. Bond. He commences by challenging three assumptions which weaken the classical theories. These neglect the work previously done on feed particles under examination although such effort is part of the total input of crushing work. Secondly the old theories were arrived at from study of breakage of cubes not of the irregularly shaped particles handled in milling. Thirdly these theories equate useful work input against energy increase on breakage and neglect the energy released as heat as wasted or external to the problem. Bond proposes a theory intended to give consistent results over all size reduction ranges for all materials and machines.

It appears that neither the Rittinger theory which is concerned only with surface nor the Kick theory which is concerned only with volume can be completely correct. Crushing and grinding are concerned both with surface and volume the absorption of evenly applied stresses is proportional to the volume concerned but breakage starts with a crack tip. Usually on the surface and the concentration of stresses on the surface motivates the formation of the crack tips.

## SECONDARY CRUSHING

### The Duty of the Section

In primary crushing the largest lumps of ore mined must be dealt with. In secondary crushing the maximum sized piece is unlikely to exceed 6 in average diameter and some of the unwanted material coming from underground has probably been removed. The feed is therefore easier to handle. The crushing machines need not have so wide a gap nor so sturdy a construction. The transporting arrangements can be less robust since the large pieces of rock have now been reduced to more manageable fragments.

Washing and sorting if practised may be done in the primary section but is more usually combined with secondary crushing where the rock is smaller and more easy to handle. Secondary crushers are usually arranged in series with the primaries so they must be able to handle similar loads. Their main task is to

reduce the ore to a size suitable for wet grinding. It then goes to the fine ore bins which must have sufficient storage capacity to receive all the ore accepted for treatment and to keep the plant running continuously although the mine only delivers its ore periodically.

### Layout and Equipment

A generalised secondary crushing scheme in which *minus 6* rock is sorted and reduced to *minus 1* in one operation or pass is shown in Fig. 1. The numbers in this flow sheet refer to

Transport and feed regulation from primary crushers to screen 2. The feeder stops starts or modifies rate of delivery and the guard magnet removes magnetic iron ahead of 4. It could be used at 3 instead of 1 or be dispensed with if hand picking were used on 3 to remove iron. This might be done where the danger of damage to 4 lay in the passage of manganese steel or other non magnetic and uncrushable material.

Separation of finished *undersize* from *plus 1* rock which is to be crushed. A robust screen system is used.

Sorting picking or transporting belt (belt conveyor). This delivers to 4 and may elevate the ore in transit so that the crushed rock leaving 4 falls by gravity to 1. The  $6 + 1$  ore is of a convenient size for handling so removal of waste and detritus is possible. The side arrow shows that provision for collection and disposal of finished waste is then needed.

Secondary crusher set to  $7/8$  By making the set a little below the 1 screen aperture re circulation of *near sized* waste is kept down

Conveyor belt or chute returning crushed ore to 2.

Conveyor belt perhaps equipped with weight recording equipment (weightometer) and automatic sampler which delivers screen under size to storage.

Fine ore bin/s where ore accepted for treatment is received and fed at a controlled rate to the plant.

The purpose of the weightometer (6) and sampler is to record the tonnage accepted for treatment and to sample it for assay grade moisture and particle size. Process control requires knowledge of dry tonnage treated and the values contained in that tonnage.

If sorting or dense media separation is also practised it will probably be introduced in this section. In the case of material requiring fine crushing by dry methods special equipment of kinds not considered in this book may follow. The fixed path crushing machines discussed in this chapter normally deliver to the bins ore crushed to below between 1 and  $\frac{1}{2}$ . Closer settings are possible particularly if the secondary crushing is performed in two stages so as to reduce mechanical strain by keeping each machine's reduction ratio below 7 to 1. The considerations which influence lay out and installed capacity include the crushability of the rock itself the question of waste elimination and the maximum rate of delivery of ore for immediate handling. During the mine's transport period the fine ore bins are filled though throughout the mill's working day (usually 24 hour) they deliver steadily to the next stage of treatment.

Secondary crushing is today characteristically performed dry. This word is used relatively as the ore may be moist or may be wetted during washing operations or when water is run in through a crusher to prevent the build up of clay. (This last is bad practice and may lead to mechanical trouble.) The machines mainly favoured are modified forms of gyratory crusher though other appliances such as crushing rolls are in limited use. Beater mills with their variants (hammer whizzer pin disintegrating and ring roll types) deal with large tonnages of coal asbestos limestone and easily broken mineral. The gravity stamp though worked with added water is briefly described in this chapter since it is a fixed path machine. It is obsolescent its place being taken by the rod mill described later but is still in use in a few older plants.

### The Symons Cone Crusher

As with the gyratory crushing results from interaction between three essential parts. The important difference is that in this case the spindle (1) is not hung from its upper end but is supported in a universal bearing below the gyrating head or cone (2). Normals to the arc through the universal bearing carrying the breaking head intersect at O. This break-ing head gyrates inside an inverted truncated cone (3) called the

bowl which flares outward and thus allows for the swell of the broken ore by providing an increasing space for it to enter after each nip has released crushed ore for a further drop. Two types are made the standard and the short head. These differ chiefly in the shape of the crushing cavities. Standard crushers deliver a crushed product varying from  $\frac{1}{4}$  up to  $2\frac{1}{2}$  usually in open circuit and can be fitted with fine medium coarse or extra coarse crushing cavities. Short head crushers have a steeper head angle a longer parallel section between cone and bowl and a narrower feed opening. They deliver a crushed product ranging from  $\frac{1}{8}$  up to  $\frac{3}{4}$  and usually work in closed circuit as in Fig.1.

The springs then return the bowl to its correct clearance. While this happens or when choked with clay the Symons crusher is apt to let oversize escape. Such clay is sometimes dealt with by introducing water with the feed. Better practice is to remove it by washing. It is dangerous with any dry crushing machine to risk the entry of abrasives into its bearings or bevel gears.

The springs which hold down the bowl yield when the load is too severe. It is therefore usual to run the cone crusher in closed circuit with a screen thus ensuring that tramp oversize is returned for further treatment. This recirculated material which may include fragments of non magnetic steel not removed by the guard magnet may call for removal by special methods.

With some ores there is a tendency for extra tough particles to spring the crusher at a slight oversize to the set. (In passing it should be noted that in all closed circuits there is selective retention of one fraction of the ore stream which may call for special measures.) A simple solution

Ratio of reduction is controlled by screwing the bowl up or down by means of its capstan and chain.

A 2 ft. standard crusher receiving  $2\frac{3}{4}$  rock is rated to deliver 15 tons/hour  $\frac{1}{4}$  open circuit or 60 tons/hour when reducing 4 feed to  $\frac{1}{2}$ . A 2 ft. short head crusher receiving  $1\frac{3}{8}$  feed and delivering  $\frac{1}{8}$  in closed circuit has a capacity of 6 tons/hour. When reducing 2 feed to  $\frac{1}{2}$  product the capacity is 20 tons/hour. The coarser 7 ft. standard crusher has a capacity of 900 tons/hour when reducing 18 rock to  $1\frac{1}{2}$ . Such general figures taken from manufacturer's literature would require checking for performance on samples of the specific ore if it was proposed to work a crushing plant at full capacity.

### Gearless Gyratories

Several crushers are marketed which avoid the complication of bevel gearing below the rock treating section by making the drive a direct extension of the rotor of the electric motor. The Newhouse which is hung from cables to absorb the vibration of its running has the motor above the grit zone. It is run at 500 to 600 r.p.m. with an eccentric throw of about  $\frac{1}{4}$ . An advantage claimed for this design is that by avoiding the use of gears little power is consumed when the machine is idling

### ROLLS

Although much work once done by rolls has been taken over by cone crushers these machines still handle a considerable tonnage. Standard

The method of feeding is important. Unless the entering ore is spread evenly over the whole width of the rolls partial wear occurs causing the surfaces to become grooved or flanged. The Taylor heavy duty crushing rolls incorporate a fleeting mechanism which causes one cylinder to move to and fro on its axis thus reducing this type of wear. A good practical rule is to arrange the feed so that some ore falls outside the crushing area at each end. This helps to even wear over the full width of each roll. Another is to raise the feeding device so that ore arrives on the rotating surfaces at their peripheral speed. This gives the best conditions for seizure. Rolls can only work as arrested crushers if lightly fed because the breaking ore swells in volume as voids are produced at the same time as the particles fall into a more restricted space. If not starvation fed rolls are choke crushers ore grinding on ore. Unless rolls of very large diameter are used the angle of nip limits reduction ratio so that a flow line may require coarse crushing rolls to be followed by fine crushing rolls. Although the floating roll is only supposed to yield to an uncrushable body the choked packing of ore in the crushing throat sets up so much pressure that the springs are usually on

the work during crushing and a moderate proportion of unfinished material is jet through. For this reason rolls should be worked in closed circuit with screens wherever control of maximum particle size leaving the crusher is important.

### Hammer Mills

In these machines which can be used either as primary or secondary crushers the breaking force is mainly due to a sharp blow applied at high speed to free falling rock. The moving parts are beaters (hammers rectangular plates hanging bars or heavy metal rings). They move in a more or less fixed circle of swift rotation though they are loosely suspended from pins on discs mounted on a driving shaft inside a robust stationary casing with a grid through which broken undersize leaves the mill. The beaters weigh from a few up to 250 lb. and the larger machines can work on feed as coarse as 8 cube. Fracture is chiefly produced by the flailing action as the beaters hit the ore as they spin at from 500 to 3 000 r.p.m. though part of Both uni directional and reversible hammer mills are manufactured. The former can be used over a wide size range of soft or friable material in both primary and secondary crushing and the latter in secondary crushing. Reversal of the rotor direction obviates the need for turning the hammers round. A hammer mill with its breaker grid arranged like a miniature belt conveyor has been developed for sticky or wet feed liable to clog a fixed grating. Material which fails to fall through climbs against the down running new feed. Another type of hammer mill the Impactor is designed to obviate stoppage for hammer adjustment. The rotor is reversible and end wear can also be taken up while running by movement of the anvil blocks which regulate the set of the mill. Elimination of a retaining grid makes the machine able to cope with frozen or sticky feed and aids quick passage. The velocity with which the blow is struck in impact crushing is the main determinant of the severity of shock loading. The vertical distance of free fall as the feed enters is therefore a control factor. Care in arranging a suitable dropping height influences product shape size and production of fines.

Among the minerals broken by this type of milling are limestone spars gypsum shale clays coal asbestos gravels and rock required for ballasting or concrete aggregates. The products are characteristically sharply fractured. Moisture affects efficiency adversely and wear on the beaters is heavy with abrasive material. Product size is controlled to some extent by varying the escape grid apertures clearance and speed. Unlike the dry crushers hitherto considered these machines are impact breakers.

## FORCES IN WET GRINDING

### Optimum Grind

Optimum size of release from the grinding circuit into the concentrating section is determined by technical and economic considerations. The finer an ore is ground the more this grinding costs. Up to a point finer grinding usually results in higher recovery of values but beyond this over grinding leads to poorer recovery. Optimum grind defines the mesh of grind at which a maximum profit is made on sales when both the working costs and the effect of grinding on the recovery of values have been brought into consideration. Such an optimum point is determined in the first place by test work in the laboratory when the flow sheet for a specific ore is being prepared. It then becomes the operator's aim to achieve maximum through-put at this optimum grind. With care and attention it is frequently possible to improve on the figures obtained in preliminary testing.

Optimum grind or *release mesh* refers to the sizing analysis of the ore particles finally leaving the grinding section. In its simplest form it can be specified as say a 100 mesh grind meaning that substantially all the particles in a carefully taken sample pass through a 100 mesh screen. A more exact optimum might call for say *minus 5%* on 100 mesh and *plus 85% minus 200 mesh* indicating that a little coarse and rather light gangue stuff may safely be allowed to leave the circuit and that the needs of the

concentrating section of the plant will be best met if overgrinding is avoided by stopping the process when 85% of the ore by weight passes a 200 mesh screen. Such a specification calls for care in order to bring all the material undersize as well as oversize between certain size limits so far as skillful control permits. It results from the scientific application of forces now to be described. Careful grinding preparation develops the latent characteristics of each mineral species it unlocks from the ore in the form of individual particles. It thus simplifies the work in the concentrating section and is of great practical importance.

When ore characteristics vary from section to section of the mine it may be found economically desirable to avoid mixing so that each type can receive specialised treatment. Separate bins are provided in such a case. Ores may also be bedded so as to be drawn in a uniform grade through one grinding circuit. In a small operation the dispatch from the mine of markedly different types of ore should be so regulated as to provide a steady run of mill head feed.

#### Applied Power

Of the electrical power fed in a loss of the order of 10% occurs in the motor and between 10% and 15% in the gears and mechanical friction of the mill. The balance is available as useful power as kinetic energy in the tumbling crop load but the fact that it is available does not by itself lead to its efficient use. If the crop load is not properly constituted part or all of this kinetic energy will be wasted by conversion to avoidable heat sound and ground up metal.

Fig. 1. shows torque (in the sense of useful power) to be nil at zero and also at critical speed. At critical speed (*plus* the extra speed necessary to compensate slipping of the crop load and hold it by centrifugal force) grinding stops.

Such a position is largely theoretical since it could not be reached in a normally charged tumbling mill. The relationship between centrifugal force and its radial tangential thrust at various depths along the mill's radius passing through the crop load precludes such seizure. The many inter-acting factors at work in the churning charge tend to confuse the picture of its dynamics. To clarify discussion consider the case (admittedly over simplified) of a variable speed mill with smooth liners no ore or water and a load of steel balls of one size. As it starts very slowly from rest the load surface tilts until the slope is reached where load stability fails and the top layers of balls slide down. Neglecting slight irregularities in breaking away the power draft is steady for a given speed when the stable displacement is at its maximum. This draft (ignoring mechanical loss outside the mill shell) corresponds with the displacement of the centre of the turning load from the vertical diameter by a distance  $a$  along the theoretical path (zero to critical) in Fig. 1. As the mill speed is increased this displacement reaches its maximum. With further speed increase the distance  $a$  begins to recede and power input falls. The concept of freeze up at critical speed is not valid in view of three main forces at work of which centrifugal fixation is only one. First before this stage is reached any peripheral balls rising clear of the down slipping load after it has passed the plane of its horizontal diameter fail to maintain tangential direction because they are now acted on by gravity. Losing contact with the shell they take a falling trajectory to the down running side of the mill. In the course of this they collide either with other balls loosening the upper part of the charge or with the shell itself thus transferring part of their kinetic energy back to the shell from which they had received it. This acts against the input of new energy once a balancing peak of flight has been passed. *Second* the packing structure of the charge changes steadily as mill speed increases. At rest ball rested on ball and voids between these spheres was at its minimum. With rising speed the core of the charge and also the upper layers are loosened so that the volume increases. For a given mill speed there is a critical volume of charge at which the centre of mass  $a$  is at its maximum displacement from the vertical diameter. If the volume of the charge had been sub critical at this speed it would have been possible to increase the out of balance loading by adding more balls and the power draft would have risen. Similarly it would have been possible to increase speed without increasing charge to obtain the same effect. If on the other hand more balls were added or speed

were increased to the super critical point the combined effect of the reduced out of balance dead loading and kinetic impact of falling balls on the down side of the shell and the toe of the load would be to reduce the useful input of kinetic energy to the system and the current or wattage drawn by the driving motor of the mill would fall. The *third* force the consolidation of the charge by centrifugal force is modified by the first two.

The practical crop load is of course a mixture of grinding media of various sizes and shapes perhaps even of varied density since steel and large pieces of ore may form part of the crushing bodies. Next there is the ore partly a new feed from dry crushing and partly a return load of partly finished sands from the closed circuit. Further there is the make up water added at mill head which modifies the plasticity of the tumbling load in accordance with its *specific surface* and the percentage of water used. Finally there are the liners of various types shapes and degrees of wear with grip modified by changes in the amount of slime or slippery sulphide mineral anointing their surfaces. Again over simplifying somewhat the crop load can be pictured as a loosely plastic body being continuously moulded into shape by tumbling action and influenced in its mass cohesiveness by the frictional hysteresis of its components. In most operating circuits the mill speed is fixed but in all the crop load varies slightly in volume with the grindability of the ore. Since only finished grind pulp is allowed to leave the grinding section increased resistance of newly entering ore results in increased retention in the closed circuit part of which takes place in the crop load. If the load then goes super critical (in terms of the above discussion) less grinding power is available less grinding is done and the overcharge increases. If more easily ground ore comes to the mill the charge is diminished and too much energy seeks too little ore in the sub critical loading which follows.

An equation for best operating speed ( $n$ ) in terms of internal stability of crop load and frictional grip from the shell has been proposed by Davis.

In a ball mill the rate at which power is converted into kinetic energy is fairly steady but in a rod mill it varies somewhat abruptly owing to entanglements hold ups and momentary seizures of the rods as they turn. If the kinetic energy is correctly applied a maximum of properly finished ore results but whether correctly applied or not the power continues to enter the mill so long as the crop load is being dynamically held out of balance. Unlike nearly all other comminuting appliances the grinding mill uses about the same amount of power all the time it is running. Substantially all the kinetic energy is finally dissipated as heat which warms the transient pulp. In the endeavour to find a fundamental expression for grinding efficiency it has been suggested that since new surface is proportional to grinding energy (Rittinger's law) and since this involves the creation of new surface tension or surface energy on the newly sheared particle surface the efficiency of grinding is measurable as the proportion of useful power to new surface. Calculations along these lines have produced several sets of figures all agreeing in the conclusion that grinding efficiency in the ball mill is very low well under 0.3%. For practical use industry needs something more concrete to measure the efficiency of its daily operation. Performance in the plant can most conveniently be judged by its relation to some selected standard of throughput. There is no good direct way of measuring the surface energy of solids. In any case the increase in surface energy of the particle which is due to the transfer of some input (grinding) energy to the newly created area is probably only part of the total rise in energy. No method exists for assessing the internal changes in energy level (physical chemical and electrical) which accompany comminution. Efficient or not the tumbling mill is the best machine at present available for the work of grinding which is the most expensive cost per ton item in the flow sheet.

Rittinger's law has been the subject of much research and may be regarded as a good approximation. The operator will work on sound lines if he thinks of grinding force as resulting in new surface (in an efficient operation). The next step is for him to ensure that

As much of this new surface as possible is created on particles neither too big nor too extravagantly small for treatment in the concentrating section

As few as possible of those particles shall consist of steel abraded from the balls and liners

As many as possible shall consist of value containing ore.

This mental approach enables him to see the problem of grinding realistically and to translate his vision into effective operational control.

Useful or Net Power

The kinetic energy generated in the crop load by transfer of driving power through the mill liners should be maintained at its peak value in order to obtain the maximum amount of grinding from the system. This maximum draft is achieved by means of a correct balance between four main factors

Speed of mill rotation expressed as % *critical speed*.

Liner grip notably of body (horizontal) liners.

Constitution of crop load or charge C (media ore and water).

Volume of C under running conditions.

First consider item *d* *a* and *b* being fixed and *c* varying only as to ratio of grinding media (*m*) to feed (consisting of new ore classifier returns and mill head water). Take as the starting point peak power draft with displacement of C to the rising side at its maximum unbalance. If C now increases part of this increased volume is re balancing the load by overspill to the down running side. It thus reduces the unbalance of C and also feeds more driving energy to the shell liners. This transferred energy does not of course increase the total input. The reduced unbalance does in fact result in a power drop registered on the ammeter of the driving motor or motors. However deployed the net input power is proportional to an exponential value of new surface produced and any reduction of this input leads to a corresponding diminution of useful grinding. This is why the mill must be run with a maximum input of useful power in order to maintain peak efficiency.

Some qualification is desirable at this point. The purpose of grinding is not solely technical. It must contribute to the maximum overall profit which depends on a balance between all processing costs and the grade and percentage recovery of concentrate in the best condition for further use. The size analysis of the solids in the mill discharge has an important bearing on subsequent treatment and grinding is a major cost item. This frequently raises the operating question of shattering *versus* abrasion in the grinding section. The fierceness of shatter at constant speed will obviously be reduced as C increases in weight and volume beyond peak displacement of its centre of mass. Slippage will then increase balls be more blanketed and impeded in falling and the toe of the charge will be more abraded and less hammered. The question always arises What kind of grind is best for a specific ore treated by a specific method? The reader should re read this section after the chapters which deal with various methods of concentration have been studied.

A change in loading volume due to variation in retention of ore upsets the balance between *m* and C and also alters the frictional characteristics of C. If C increases shatter is reduced and the coarser particles of ore are less adequately reduced to sizes which *m* can seize and abrade. At the same time the specific surface of C decrease though no change has been made in the carefully controlled solid liquid ratio which *K* being maintained in relation to optimum specific surface. From this point there is cumulative deterioration in the efficiency of comminution. Slowly the mill discharge size analysis increases its percentage of coarse material. This discharge is returned by the closed circuit classifying system in increased volume though there has been no increase in new feed of ore. Thus both C's texture and volume are changing from their optimum balance at an increasing rate. This readily observed connexion between reduced power consumption and loss of grinding efficiency (which may have adverse effects right down the flow line if it leads to overloading with wrongly ground material) underlines the vital importance of a well controlled grinding section.

Hence *a* and *b* may now be related to this discussion. When mill speed is increased without any other

alteration C is reduced and *vice versa*. This fact was brought out clearly in the Vassbo experimental work referred to earlier. There the mill's best performance in overall terms was found to be 60% critical speed. Taking this 60% as the index of 100% efficiency each increase of 1 % of speed was accompanied by a drop of 1 % or so in efficiency. At 80% critical it was necessary to use 25% more power to do the same amount of grinding. This extra power was obtained by increased unbalance of the crop load. The point is significant since it shows that maximum unbalance (accompanied by maximum draft of useful power) cannot be taken in isolation as the criterion of efficiency. In this case it showed that the mill was too big for its job and in consequence its diameter has since been reduced. Maximum power draft must be related to the required finished grind and achieved by the correct composition and volume of C. In the Vassbo operation autogenous grinding and a variable speed mill were used with automatic linkage between speed and change in the volume of returned circulating load. With ore as m change in size composition of m components is far faster than with steel balls and variation is easier to arrange and observe. The work was done on a full working scale and tied in with the sub-sequent treatment so that effects on recovery could also be seen. The interacting factors thus revealed should affect grinding research and development. A few further points may now be noted as accessory to the above discussion. When the volume is steady the net power is highest with the interstices between balls full of ore and lowest with them full of water which has a much lower density and therefore reduces the total crop weight. Power used is higher with plenty of sharp sand in the crop than with slimy sand only since the extra friction helps the liners to grip the load more firmly and raise it higher. It is higher with a low discharge mill because pulp rises centrifugally on the rising side but can escape near the periphery of the grate whereas in the high discharge mill it can only overflow from the trunnion so that a larger volume of pulp must be retained on the falling side of the mill. A drop in the ammeter reading of power input to a low discharge mill might show that the discharge grates were partly clogged.

## DRY GRINDING

### Preliminary

Though most ores are reduced by wet grinding before being processed some can better be ground and treated dry. Many minerals and synthetic substances require size reduction only. Other grinding problems arise in which chemical instability contamination corrosion or risk of explosion call for special precautions such as milling in an inert atmosphere or one where moisture is undesirable or must be removed. In an arid country the chronic shortage of water may dictate the use of dry grinding methods. Where a dry end product is called for and can be processed up to the re-quired state without the use of water dry grinding is to be preferred. Among the raw materials thus treated are asbestos rock and crudy coal for powdered fuel cement clinker talc metal powders drugs and chemical salts. In addition to open and closed circuit grinding batch treatment is frequently used. In this method grinding media and feed are loaded into the grinding mill and worked dry until the desired state of attrition has been achieved. The product is then discharged.

In the treatment of ores by chemical methods such as the cyanide process experimental dry grinding has shown promise. When comminution is followed by froth flotation it is usual to protect the newly developed mineral surfaces and this is best done by grinding under water to which any required protecting chemicals can be added. The technical applications of dry grinding in mineral dressing are at present limited by this consideration.

### Fixed path Mills

Taggart classifies dry mills into two groups in which the comminuting elements are relatively few and follow definite paths (fixed path mills) and those in which the elements are multifarious and not

constrained as to individual paths (tumbling mills) . The latter do the bulk of industrial dry grinding but the former of which there are several types handle an important tonnage.

Burr mills range from the old fashioned grindstone originally used in grinding cereals to vertical types. Two discs of stone either horizontal or upright are rotated in opposite directions or worked with the lower one fixed and the upper revolving. Feed is central and finds its way along grooves in the stone faces maintained by stone dressing to a peripheral discharge. The material is ground by attrition during its journey being dragged between the stone faces. Soft rocks such as clays barytes talc lime and limestone and gypsum are treated in these mills. Feed is minus  $\frac{1}{4}$  and discharge can be as fine as minus 200 mesh. The mills are used for grinding material not likely to be injured by frictional heat and also where staining by iron must be avoided. Care must be used to keep hard or uncrushable material out of the feed.

Developments of this principle include vertical disc mills with steel grinding faces. The laboratory disc grinder is widely used. Its discs can be parallel or slightly offset to one another the latter arrangement reducing choke and improving throughput. Capacity is low.

Hammer mills and rolls were discussed with intermediate crushers. They can also be used for fine grinding. A special application of the hammer mill is in the crushing of asbestos. The requirements are unusual in that the material as mined carries the valuable fibre sandwiched between layers of shale. Hammer mills with heavy manganese steel plates are used to fiberize the blocky fibrous rock. The beating action opens the fibres and loosens attached shale. This is thus reduced to a fine grit which can be screened away.

The Raymond Impax Pulveriser introduces material through a roll feeder to the grinding chamber which is swept through by an air stream. The air entrains finished material and dust and carries them to a collecting cyclone and dust collecting chamber. A further refinement in fine grinding by hammer milling is reported by Robertson. This is a two stage mill in which the runners in the second chamber have a higher peripheral speed at which they complete the work transferred from the first chamber.

The jet pulveriser or microniser carries a feed of  $\frac{1}{8}$  material in air or steam at a pressure of about 100lb./sq. in. This streams out through suitable circular expanding chambers from its tangential delivery. Extremely fine grinding results partly by mutual jostling between the solid particles partly by contact with the chamber walls and by pressure release. Finished fine product is discharged from the centre at sizes varying down to one or two microns. The capacity is good but wear is heavy and the mill is limited to specialised work.

Edge runners resemble Chilean mills with the mode of motion reversed since the rollers remain stationary while the disc on which they bear revolves. The rollers are spring loaded. They and the disc may be made of ceramic material. Plain iron and perforated iron are also used. These mills are used to treat clays and ceramics. One form is the German Loesche Mill from which the Hardinge disc roll mill has been adapted. In this two conic section rolls ride above a revolving horizontal disc. This disc table on which the ore arrives centrally runs at a speed just below that at which peripheral discharge of crushed material begins. A dam forms round the circumference over which the discharging material is pushed by arriving feed and falls into a classifying air stream which lifts finished mineral and returns anything coarser to the grinding disc. In the Lopulco mill there are either two or three spring loaded conic rollers. These mills range in output from 1 to 50 tons/hour and are designed for low medium or high speed. There is external provision for adjustment of clearance between the rotating table and the rolls which cannot make direct contact. The feed receives both loaded crushing and shearing attrition. An exhaust fan maintains air sweeping and removes finished product. In addition to its wide use in producing powdered coal this mill grinds a variety of softish minerals substantially through 100 mesh. The list includes gypsum lime phosphate rock and various industrial earths.

The older pendulum or roller mills include the Huntington and the Griffin. In both one or more pendulums revolve inside a wearing ring against which they bear owing to the centrifugal force set up by their rotation.

Material trapped between roller and ring is ground till it escapes through guarding screens set peripherally. In the Williams mill three to five rollers are pressed outward in similar manner but the mill is swept through by a current of air which carries to a collecting cyclone or air filtering arrangement all particles small enough to be borne along. The air or gas can be preheated in a furnace and natural draught is aided by an exhaust fan above the grinding compartment. In the Raymond bowl mill which is used for producing pulverised coal the bowl rotates against spring loaded mullers and finished material is removed by a current of air. The Babcock and Wilcox machine has balls rotating in a horizontal grinding ring where they press on and pulverise material fed down into the ring the finished product dropping by gravity to an external classifier. In a variation the mill is swept by air or gas hot if necessary discharge being upward. Where air sweeping is used hot air can be used for the purpose of drying the feed.

### The Vibrating Mill

Intermediate between the fixed path and the fully tumbling mill is the vibrating ball mill. This has not changed importantly since its prototypes were developed in the United States and Germany in the pre war period. An industrial model now in increasing use as described by Paricio is nearly 6 high  $9\frac{1}{2}$  long and 7 wide. It weighs six tons and is vibrated by the un-balanced rotation of eccentrics driven by two 50 h.p. motors at 1 200 r.p.m. The layout consists of a grinding cylinder rigidly attached to eccentric mechanisms in independent horizontal cylinders parallel with it. This assembly is mounted on four sturdy vertical springs and vibrates with an amplitude of  $\frac{3}{4}$ . In action the grinding media have a vibrating period of about 1 160 r.p.m. and occupy about 80% of the mill's volume. The load tends to rotate. For suitable ores this system has proved versatile and cheap in standing space cost of installation weight and maintenance. A 30 dia-meter mill reduces *minus*  $\frac{1}{4}$  soft and friable feed to 99% *minus* 325 mesh at a rate of  $2\frac{1}{2}$  tons/hour. Feed and make up media enter through a dust tight flexible spout and are discharged *via* a retaining grate. This mill can also be worked wet and the retention time can vary from one minute up. When used for batch grinding two receiving tanks are used and the material is worked through from one to the other and then back until the required fineness is reached.

Vibration milling has met the need for grinding metallic powders to sub micronic sizes in an inert atmosphere and handles such inflammable elements in this way as aluminium and magnesium. Capacities quoted range on limestone and using steel balls from 1 ton hourly in the 15 diameter mill to 15 tons in the 42. an 80% *minus* 4 mesh feed being reduced to 80% *minus* 200 mesh. Where iron in the product is inadmissible alumina balls and special linings are available. Materials handled commercially include tungsten carbide aluminous nickel silicon carbide and iron oxide.

### Tumbling Mills

Dry ball mills have much in common with those described in Chapter 5 but there are marked differences in the method of operation. Continuous and batch grinding are practised sometimes with rods as grinding media but more usually with balls or autogenous crushing bodies.

Since batch treatment mills are not limited in design to types which can be fed at one end and discharged from the other a variety of shapes are in use cylindrical conico cylindrical oval polygonal and even cubic. The liners and crushing media can be made of iron or ceramics according to the requirement of the work. Feed and discharge are usually made *via* an aperture in the shell a screen being placed over it to retain crushing media during discharge. The mill is charged run for a suitable period stopped opened and emptied.

The ball load is kept lower in dry than in wet grinding below 40% to avoid over carry at cataracting speeds which would cause the flying balls to hit the down running side.

One of the older methods of ensuring fineness in dry grinding is to divide the ball mill into two or more compartments. These are separated by grates which retain the material in the compartment for which crop loading is most suitable until it can pass through the grate and be elevated by scoops to the next. The

Hardinge Tricone Compartment mill uses the back slope of its first (conic) section to promote media segregation and makes it possible to dispense with the third section shown in Fig 5.

In an air swept single compartment mill which has gained considerable favour in the preparation of pulverised coal the difficulty of maintaining a gradient through the long cone of the Hardinge is partly overcome by using a retaining grate toward the discharge end. Behind this lifters pick up the undersize and drop it into the classifying stream of air sweeping through the mill.

Pilot tests show one step comminution to use less power than a conventional crushing and grinding sequence and to favour medium and fine-grained ores which require finer finished grinding where air sweeping is more effective. Ore tends to disintegrate selectively along grain boundaries and to produce mineral species at their natural grain size. Any such effect assists subsequent concentration. Liberation appears better than with rod milling and wear is less. If selective grinding accompanies quick passage through the mill the later treatment benefits by having less over-ground particles to deal with. The Swedish tests suggest that when working for a coarser liberation mesh air sweeping is not fully effective. Tests at Doorn fontein showed higher recovery both of gold and uranium after 24 hour laboratory leaching of *minus* 200 mesh banket ore crushed direct from run of mine feed than of various samples drawn from the conventional flow line. With a steady increase in the chemical extraction of values from their ores this improvement which again suggests disintegration along grain boundaries attracts the interest of process research.

Under normal weather conditions Weston considers a moisture content in the feed tolerable up to 3½% but in sub zero temperatures external heat to be needed from 1½%. Installed capital costs are lower than for comparable wet grinding and maintenance is much lower.

It is used in dry grinding in the same general way.

### Operation

The moisture content of the feed is an important factor in dry milling. If nothing is done to classify a circulating load a very small percentage of water (½% to 1¼%) ruins fine grinding. If the circuit is closed through fine screens a little more moisture can be tolerated without clogging the screen apertures unless the material is soft and clinging. The temperature of the circulating air rises as the ore is milled and its humidity increases when it picks up moisture from the passing feed. Enough air must be bled off to avoid saturation and thus ensure that this transfer of moisture can continue. The heat requirement for drying changes with the season and must be supplied by warming the air when necessary. The water content affects grinding cling in the crop load cushioning cataracting coating of crushing media and mobility and classification of partly finished material in the closed circuit. As with wet grinding work the mill capacity required for a given rate of throughput depends on the grindability of the ore and on the sizing analyses of feed and finished product. The finer the grinding is taken the lower will be the tonnage treated. Removal of finished material is very important to high capacity. If it is allowed to remain in the mill it deadens the grinding force by packing the interstices. It diverts what should be grinding energy to the task of re-distributing the crop load and of overcoming its frictional resistance and cling. This though it adds to the heat of milling contributes little or nothing to the comminution of the larger particles. Where a fairly coarse final grind is wanted (in say the 20 mesh zone) screening affords positive separation since at this size a lively open load can be worked over screens without blinding. (Blinding connotes the wedging of an oversized particle into a screen aperture thus putting it out of service and it becomes serious with clinging material on small screens.) This coarseness calls for strong air currents to sweep finished material out of the mill and a mill design which includes retaining grates followed by lifters to the discharge overflow may be needed.

## WET GRINDING MILLS

## Preliminary

The general term *tumbling mill* includes the *rod mill*, *pebble mill* and *ball mill*. It is of cylindrical or cylindrical conical shape and rotates about a horizontal axis. A load of crushing bodies called the *grinding media* forms part of the *crop load*. They bear upon the piece of ore in the tumbling mixture with abrasive and/or impacting force sufficient to reduce the mineral to particles of the desired size. As in the case of dry crushing grinding may be divided into two stages primary and secondary if the scale of operation justifies such elaboration. Milling speeds (r.p.m. and rate of feed) types of liner and size and shape of crushing bodies are chosen to develop shattering or impact milling in the primary mill and a more gentle abrasive action in the secondary one. The object is to bring the ore to the *mesh of grind* called for by the concentrating section of the mill and this is best done in separately controlled stages. Often the primary grinding mills must work vigorously on a quickly passing stream of ore and the secondaries more gently and with longer retention of the pulp.

### Types of Mill

Tumbling mills may be classified according to shape into two types cylindrical and cylindro conical. In the latter two cones are joined by a cylindrical section. At the feed end is a flat cone. After passing the zone of maximum diameter sometimes called the *drum* the pulp climbs a steep cone to the discharge. This shape has been adopted in the *Hardinge mill* to develop specialised grinding forces at each stage of the passage of the feed suited to its changing condition as it progressively disintegrates. Another and perhaps preferable classification of mills is into two types high discharge and low discharge. From Figs. 2. and 3. it will be seen that although the feed enters through a hollow trunnion at the centre of the feed end the discharge arrangements are very different in the two types. In the high discharge mill the only possible down gradient is a larger trunnion at the discharge than at the feed end so that in effect pulp only leaves the mill because it has been displaced by entering feed. In the low discharge mill the support of a hollow trunnion at the discharge effect is either avoided in design or lifting scoops are used so that a gradient through the mill is created from feed to discharge. In addition to displacement of discharge by entering feed this adds the effect of gradient to accelerate passage of pulp through the mill at a more or less controlled speed. Since grinding force is applied at an even rate the faster the ore passes through the mill the coarser is the discharged product.

In the type illustrated in Fig.3. the feed introduced through the scoop at *A* is retained in the crop by the grating *C*. Material sufficiently fine to pass through this grating is elevated by the radial lifters to the overflow trunnion *B*. In another and heavier form of construction the discharge end is not hung on a trunnion but supported on rollers by means of a steel type which encircles the mill shell. The mill discharge can then flow straight out.

It is usual to say that the *Hardinge* is high discharge only but this statement fails to take account of the effect of the steep cone. The effluent of a mill consists of ore and water flowing as pulp. While it is true that this pulp must climb to the discharge trunnion of the *Hardinge* it is also the fact that the cross section of the flowing stream is continuously shrinking so that the pulp stream must run faster and faster as it flows toward the

One type of mill little used today is the *Krupp screen faced cylindrical mill* with peripheral discharge. In this machine the feed is introduced through a trunnion and discharged when it has been ground sufficiently to pass through the fine screens lining the cylindrical part of the mill. Heavy perforated plates protect these screens from injury and a coarse screen is mounted concentrically inside each fine one to give further protection. External sprays provide water and the external casing can be flooded so that the mill dips into water.

### The Hardinge Mill

The shell of this mill consists of a flat cone followed by a drum with a steep cone at the discharge end. The shell is carried in two hollow trunnion bearings which permit feed and discharge. Drive is by a crown wheel bolted round the steep cone and driven by a pinion. The gear may be straight single helix or double helix. Straight or double helix are to be preferred since no end thrust is set up in operation. Feed may be introduced direct into the feed end trunnion or more usually through a feed scoop which gathers ore from the bottom of a feed launder and elevates it to the entrance level. The latter arrangement is particularly useful when the mill is in closed circuit with a mechanical classifier. This is a power driven appliance which sorts ore particles discharged from the mill returning the coarse ones (oversize) for further grinding and allowing the finer ones to overflow as a pulp to the next section. To effect this return (close circuit the oversize) the returning sands must gain height. They are raked up slope and discharged so as to gravitate to the gathering scoop which lifts them together with new feed to the entry trunnion. This trunnion may have a wearing plate with a conveying spiral to force the feed forward into the body of the mill.

A retaining grid can be used at the discharge end permitting the mill to be loaded nearly to the centre line without risk of discharging balls. The interior of the shell is protected from direct contact with ore by cast iron or steel lining plates called liners. For the cones segmental sections are used and for the drum portion curving rectangular liners. They may be backed with plastic material such as rubber sheet or old belting or fitted directly on to the shell. The liners are held in place by liner bolts kept tight by external nuts and rendered leak proof by plastic washers.

These mills are listed according to the diameter and width of the drum. A small Hardinge has a drum 2 in diameter by 8 wide weighs over half a ton and when loaded to half volume carries over 4 ton of steel balls. A large mill is 12 by 72 weighs 62 tons including 27 tons for its set of unworn liners and carries a ball load of over 50 tons. A 2 h.p. motor would drive the small mill but between 700 and 800 h.p. are needed for the large one. The power needed per ton of ball load rises with drum diameter and is some-where between 9 and 15 h.p. per ton of balls at *75% critical speed*.

The critical speed of a mill is in r.p.m. when  $d$  is the mill diameter in feet less the diameter of the largest ball in the crop load.

Critical speed being a function of peripheral speed the rate at which these mills can be run depends on the maximum diameter inside fully worn liners. Centrifugal effect is strongest in the drum section where the ability of the mill to lift its crop load up the rising side of the mill is therefore highest. At the same time the load inside the steep cone tends to work back down slope so the resultant is a pronounced heaping up of load in the drum and a tapering off toward the discharge. Another differentiating action is also at work as in all ball mills. The largest balls tend to work to the top of the crop load with the largest lumps of ore. They are then freest to roll or slide down slope on top of the turning load where they then are most liable to be caught between the bottom of the sliding mass and the downward moving liners. There is thus a tendency for the biggest balls and rock to work to the periphery of the drum section. The makers of this mill claim that the balls segregate themselves somewhat in such wise that the biggest are in the drum and so disposed that when they rise in the turning load they fly or tumble the furthest distance while the smallest balls work up toward the discharge. Any such tendency is useful since it causes the biggest balls to work upon the newly entered and therefore biggest pieces of ore while the smaller balls with less interstitial space handle the partly finished material as it works its way out. At low speeds the pressure of the heap piled up in the drum has crushing value and at high speeds balls break clear and rain hammering blows on the mass of churning metal and rock several feet below giving impact crushing. It is obviously of value to be able so to speak to control one's punches and to use a heavy weight against a tough piece of ore with some selectivity of target while keeping the light hits and tight jostling for the small stuff which does not need such strong treatment. The effect of the conical shape of the Hardinge mill on peripheral speed and kinetic energy on the crop load at various cross sections is illustrated in Fig. 1.

In the attempt to increase the tendency toward segregation of the largest balls at the extreme radius the Hardinge Co. also market the Tricone mill in which the drum instead of being truly cylindrical has a slight back slope toward the feed end.

#### The Low discharge Cylindrical Mill

Two types of low discharge mill are available. In both the feed end is served by a hollow trunnion which supports part of the weight and through which ore and water can either be fed by gravity or wormed in by scoop. At the far end the problem of permitting pulp to discharge at nearly the full diameter of the mill has been solved by two alternative types of construction. In one the weight of the discharge end is taken by a tyre mounted on rollers thus leaving the whole end of the mill free for a bolted on retaining grate or a loosely fitting stationary door which when closed leaves an annular gap through which pulp can escape once its solid fraction is small enough. In the other type a high discharge trunnion is the supporting member an internal grating with lifting scoops behind it serving to evacuate everything passing through that grating. The grate aperture is chosen at the size at which it is desired to pass worn balls out of the mill and varies from  $\frac{1}{4}$  to 1. Grates are cast with a slight flare outward to avoid blinding and are procurable in high grade alloy steel. The size of the mill is limited at present by manufacturing possibility. 10 by 10 mills carrying a 45 ton ball charge and using 800 h.p. are in use. A characteristic feature of the low discharge mill is that the diameter is made as great as possible while length is either about the same as the diameter or at most twice as great. This follows logically when it is appreciated that the purpose of low discharge milling is to cut down the dwelling time in the mill. A mill in which diameter and length are approximately equal is called a square mill in the United States.

#### Tube or High discharge Mills

Any low discharge mill can be converted wholly or partly to high discharge by suitably plugging the outlet end but a better appreciation of the difference between the types is suggested by Taggart who states that modern practice tends to apply and confine the name (*tube mill*) to cylindrical mills with a length diameter ratio greater than 2. They were developed according to Truscott from the Cornish barrel pulveriser which was used to liberate cassiterite middlings and from cement grinding mills and were adapted to the needs of cyanidation practice on the Rand. Before the use now universal of closed circuit grinding (in which circulation of the ore through the mill and classifier is continued until the latter permits it to leave the circuit) it was of paramount importance that all the auriferous pyrite should be so finely ground as to expose its burden of gold to the chemicals used for its dissolution. The tube mill was therefore made long. In the modern form these machines are from  $5\frac{1}{2}$  to  $6\frac{1}{2}$  in diameter up to 22 long and are loaded with such crushing bodies as pebbles mine rock steel balls or steel scrap.

#### The Cascade Mill

This recent addition to the range of wet grinding mills departs radically in shape from those thus far considered. Like the *autogenous* dry grinding Aerofall mill it has a high diameter/length ratio in this case 3 to 1. Slightly concave liners give maximum diameter at the centre of the drum. This directs the crop load away from the vertical sides a process aided by deflectors. The mill is made with diameters ranging from 6 to 36 the latter needing up to 6 000 h.p. Feed and discharge are through two support trunnions finished pulp being lifted to the latter after being ground small enough to pass through a retaining grate.

The vibrating ball mill is finding increasing use in industry particularly where an inert grinding atmosphere must be maintained.

Body liners receive heavier punishment than end liners and wear down about twice as fast. A contributory cause of wear is chemical corrosion either due to mine water or acid from decomposition of sulphide minerals. Fortunately it is frequently necessary to add lime in the mill circuit for reasons connected with the concentration processes and this gives protection to the ironwork of the mill neutralising any acids present. Although the purpose of grinding is the comminution of ore only the forces employed also act on

lining and contents of the mill and all are subjected to the grinding action. Liners and crushing bodies are therefore selected for their hardness, toughness, and resistance to such wear. When made of alloy steel they must not introduce any element into the circuit which can cause trouble in the concentrating section since the steel abrades during grinding and is carried forward to that section. Consumption of steel and cast iron liners varies and is usually of the order of 0.03 to 0.3 lb. per ton of new feed.

Observations made by Bond in which an experimental glass ended mill loaded with  $\frac{1}{2}$  steel balls but no ore showed that slipping in the layer of balls next the smooth shell increased with the milling speed in the 60% to 80% critical range whether the mill was run wet or dry. This effect in a 12" diameter mill not containing mineral would not necessarily be repeated under normal operating conditions. Abrasive grinding is proportional to slipping of the charge. Bond's observations showed 15% slip between the outermost layer of balls and the smooth liners and a further amount varying from 5% to 10% with each next layer radially inward to the fifth or sixth layer where observation was not possible.

# Uranium

## Introduction

The element uranium was discovered in Klaproth in 1789. Metallic uranium was first prepared successfully over a hundred years ago by Peligot who showed that the substance discovered by Klaproth was the oxide and that reduction to metal was much more difficult than had previously been believed. An interesting history of uranium metal production has been given by Wilhelm. Uranium and its compounds have been of slight commercial interest however until the recent use of uranium in nuclear applications.

Uranium is the basic nuclear fuel since it contains the only naturally occurring fissionable material. In these nuclear applications the element uranium is of interest because of its nuclear properties providing energy fission products and more fissionable material. Uranium is not important as a metallic material except insofar as the metal is a convenient form for use in nuclear reactors because it can be fabricated like other metals and has attractive properties such as high density and thermal conductivity. Special problems arise in the processing of metallic uranium because of its chemical reactivity, radioactivity with consequent health hazards and anisotropy. Nevertheless the advanced technology developed for the use of uranium as a nuclear fuel has yielded many tons of uranium in various forms by means of fairly conventional processing. No other metal has ever had its technology so intensively developed over such a short period of time. A large body of information is now available in the unclassified literature.

## Isotopes and Nuclear Reactions

For nuclear applications consideration must be given to the differences in nuclear reactions of the various uranium isotopes. These differences are important enough to justify large scale separation of the isotopes primarily to concentrate the fissionable uranium 235.

The properties of natural uranium tabulated below must be considered.

Artificial isotopes with mass numbers from 228 to 239 have been prepared. The most important of these is uranium 233 prepared from the reaction of neutrons with thorium 232 and amenable to fission (f 52c).

The plutonium and uranium 233 are separated from their respective precursors uranium and thorium by chemical means since different chemical elements are involved. The separation of the fissionable uranium 235 from natural uranium requires other methods. The principal method for enrichment of uranium 235 is gaseous diffusion originally carried out on a large scale at Oak Ridge Tennessee and now also at Paducah Kentucky and Portsmouth Ohio. These three plants involve a capital investment of nearly \$3 billion and consume 7 per cent of the electrical power generated in this country.

## OCCURRENCE AND SOURCES

Abundance data for uranium have to be revised upward as a result of new discoveries stimulated by the

incentives for more exploration. Uranium geology exploration and development through the world are still very young in spite of the tremendous effort that has been put into them in the past few years. The data on uranium's concentration in the earth's crust (2 to 4 ppm) show that it is about as abundant as beryllium, arsenic, molybdenum, and tantalum. Uranium is more abundant than gold, platinum, silver, cadmium, bismuth, and mercury. Uranium is widely distributed geologically and also is dispersed, being less concentrated in ores than are other elements of comparable abundance. The bulk of uranium in the earth's crust is believed to be concentrated in a narrow surface zone.

Detailed listings of various uranium minerals are available. Information on the minerals of major economic significance is summarized in Table 1. Some important uranium deposits are classified in Table 2.

Originally, the United States obtained its uranium from foreign sources, notably the Belgian Congo and Canada. In recent years, domestic sources have been developed to the point where the United States is probably the leading producer of the Western world. Another important source is the slime residue from gold production in the Union of South Africa (Witwatersrand).

Uranium can also be recovered from other domestic materials such as phosphate rock, lignite, shale, and monazite sands. Recovery processes have been developed for these marginal sources but are not being applied. With the development of various sources of uranium, notably in the Colorado Plateau, the availability of uranium is not a limiting factor in the development of nuclear reactors.

## PRODUCTION AND ECONOMIC STATISTICS

In prewar days, before the development of uranium as a source of energy or fissionable material, consumption of uranium compounds was discussed in pounds. This unit is still applicable in the discussion of nonenergy uses of this element. The market provided by these nonenergy uses was too low to justify mining operations primarily for uranium.

Several figures pertaining to the cost of uranium are worth noting. The Atomic Energy Commission has guaranteed a price of U<sub>3</sub>O<sub>8</sub> concentrate. Its price for normal uranium metal billets of normal isotopic content (0.7115 per cent uranium 235) is 840/ kg (818.18 lb). Enriched uranium is distributed as the liquefied gas uranium hexafluoride (UF<sub>4</sub> in steel cylinders). The price per total uranium content or per uranium 235 content is a function of the enrichment, i.e., the weight fraction of uranium 235. Several examples of the prices are given in Table 4. It is apparent that the cost of highly enriched uranium metal approaches 810 00/lb.

Processing of ores with minerals such as carnotite, containing a high proportion of vanadium, continues to provide a source of vanadium for which such ores were primarily processed originally.

The wide variety of uranium ores necessitates a diversity of mill flowsheets adapted to the particular ore. The processing steps and the options available to the mill operator are summarized in Table 5. A simplified flow scheme is represented in Figure 1. Detailed information on the various steps is given in an authoritative work. This volume also includes comprehensive descriptions of mills operating in the principal uranium ore bearing regions of the United States, Canada, and South Africa.

Because of the small quantity of uranium in the ore, concentration is generally carried out near the source of the ore to minimize shipping costs. The capacity of a mill is from several hundred to several thousand tons of ore/day. Convenient tabulations of domestic mills, almost all privately owned, are available.

## REFINING

The uranium concentrate has to be refined to remove the remaining impurities and yield a pure oxide suitable for subsequent conversion through UF<sub>4</sub> to metal for reactor fuel or to UF<sub>6</sub> for an isotope separation plant. The concentrate is shipped to a feed material processing plant where both the refining and final conversion to metal are carried out. Fairly conventional chemical operations are employed in the refining but, since neutron absorbing impurities are harmful even at the level of parts per million, the quality

standards are more demanding than those usually encountered in metallurgical processing.

The concentrate is first dissolved in nitric acid to obtain a solution of uranyl nitrate  $\text{UO}_2(\text{NO}_3)_2$ . This compound is soluble in various organic solvents such as diethyl ether, methyl isobutyl ketone (hexone) and tributyl phosphate (TBP). These solvents can be used to extract the uranyl nitrate which is then re-extracted into water. The aqueous solution can be concentrated and evaporated to uranyl nitrate hexahydrate (UNH) which is calcined to uranium trioxide  $\text{UO}_3$ . This oxide can also be obtained by calcination of  $(\text{NH}_4)_2\text{U}_2\text{O}_7$  precipitated from the uranyl nitrate solution. An alternate sequence involves direct precipitation of  $\text{UO}_4$  with hydrogen peroxide. The  $\text{UO}_3$  or  $\text{UO}_4$  is then reduced by hydrogen or ammonia to (brown oxide)  $\text{UO}_2$ . This  $\text{UO}_2$  may be the form in which uranium is used as fuel. Otherwise it can be treated with hydrogen fluoride to obtain  $\text{UF}_4$  (green salt). An alternative procedure involves reaction of  $\text{UO}_2$  with  $\text{NH}_4\text{HF}_2$  to obtain  $\text{NH}_4\text{UF}_2$  which is decomposed to  $\text{UF}_4$  and  $\text{NH}_4\text{F}$  which can be recycled. The  $\text{UF}_4$  is the uranium compound used for reduction to metal. It may alternatively be treated with fluorine to obtain  $\text{UF}_6$  to be fed to a gaseous diffusion plant where the uranium isotopes are separated.

Feed material processing plants employing the above sequence involving purification of uranium nitrate and generation of pure  $\text{UO}_3$  are operated by Mallinckrodt Chemical Works at St. Louis and Weldon Springs Missouri at Fernald Ohio. General Chemical Division of Allied Chemical Corp. is using at Metropolis Illinois a process developed at Argonne National Laboratory for more direct preparation of  $\text{UF}_6$  from the concentrate without going through nitrate and  $\text{UO}_3$ . The sequence of operations applied to the concentrate resembles that ordinarily applied to refined  $\text{UO}_3$  obtained from purified uranyl nitrate reduction to  $\text{UO}_2$  hydrofluorination to  $\text{U}_4$  and fluorination to  $\text{UF}_6$ . Fluidization effects reaction between the solid and the gas in each step. Refining is achieved by fractional distillation of the crude  $\text{UF}_6$ . It is also possible to precipitate  $\text{UF}_4$  directly from an aqueous solution by catalytic reduction.

Processes involving nitric acid and uranyl nitrate are used in scrap recovery carried out mainly at Fernald and in the aqueous processing of irradiated fuel.

## PREPARATION OF METAL

Pure uranium metal is difficult to prepare because of the element's affinity for other elements such as oxygen, halogens, nitrogen, and carbon. Drastic means of reduction are needed to obtain the metal from stable compounds such as oxides and halides. The reduction has to be performed in closed systems to avoid atmospheric contamination. Some of the problems involved in various reduction schemes are better understood with the help of tabulations of boiling points of the reactants, melting points of the products, and free energy and enthalpy changes for the reactions.

The large negative free energy of formation of  $\text{UO}_2$  [-123 kcal/g atom of oxygen at 25°C (77°F)] shows the need for strong reducing agents if  $\text{UO}_2$  is to be used as starting material in the preparation of the metal. Hydrogen would require a very high  $\text{H}_2/\text{H}_2\text{O}$  ratio in the gas and cannot be considered a practical reducing agent. Reduction with carbon requires vacuum and leads to contamination by carbide. Calcium is the most favourable reducing agent thermodynamically but the heat generation is still so low as to render difficult the separation of the metal and the lime by-product. The resulting metal is therefore rather finely subdivided (globules or powder). A halide flux may be added to improve lime removal and thereby obtain coarser metal. Calcium hydride can also be used for the reduction. The metals magnesium, sodium, and potassium are so volatile as to distill from the reaction zone. Aluminium can reduce oxides but is likely to form alloys with uranium. Since uranium-aluminium alloys are used for nuclear fuels, reduction with excess aluminium offers a means of obtaining such alloys directly.

Halides are more suitable than oxides as starting materials for metal preparation. Additional heat is evolved and the halide by-product has a lower melting point. This halide therefore melts and permits the dense uranium metal to settle. Massive metal (biscuit or derby) is thus recovered in relatively high purity.

with low losses. In practice  $UF_4$  is preferred over the more hygroscopic  $UCl_4$  as the starting material.  $Na_2UCl_6$  has been used because it is less hygroscopic than  $UCl_4$ . In this country magnesium is the standard reducing agent being obtainable in high purity at low cost. It is also being used in England now. The Ames process developed by Spedding, Wilhelm, and co-workers at Iowa State College the use of a sealed bomb because magnesium's high vapour pressure at temperatures attained during the reaction. The steel bomb 15 in. in diameter by 40 to 45 in. high for over 200 lb of uranium is provided with a 1 in. refractory liner thin enough to permit influx of heat during the preheating period that precedes the reaction yet thick enough to prevent overheating of the steel by the heat of reaction. Originally electrically fused dolomite lime ( $MgO \cdot CaO$ ) was used for the liner. It has been replaced by magnesium fluoride recovered as by-product of the reduction. Reduction can be carried out on a large scale (e.g. 1½ tons) to give large castings (ingot direct ingot) not requiring remelting before further fabrication.

In Europe calcium is the preferred reductant for commercial production of uranium via halides. More heat is evolved than with magnesium and the volatility of calcium is low enough to permit reduction at atmospheric pressure. Calcium was used before magnesium in this country at Ames and at the National Bureau of Standards. Calcium is also used in the United States with an iodine booster for enriched metal when high yield is an overriding consideration. Potassium was used in the first preparation of metallic uranium by Peligot and sodium can also be used. Others have applied these reductants on a laboratory scale but they hardly lend themselves to large scale operation because of their high vapour pressures. Fused salt electrolysis at Westinghouse provided the first uranium metal used at the Metallurgical Laboratory. (No evidence is available of feasibility of electrodeposition from an aqueous solution. Organic solvents have been studied with inconclusive results.) The Westinghouse process involves electrolysis at 900°C (1652°F) of  $KUF_5$  or  $UF_4$  dissolved in molten 80/20  $CaCl_2 \cdot NaCl$ . The metal is deposited as powder on a molybdenum cathode and has to be leached to remove adhering electrolyte. This process provided 65 tons of metal by the fall of 1943 when it was superseded by the Ames process. Bomb reduction has prevailed for commercial production and electrolytic processes with various modifications are used only for special purposes. An electrolyte based on  $UCl_3$  or  $UF_4$  in  $LiCl \cdot KCl$  eutectic has been developed at Argonne National Laboratory for the electrorefining of high purity uranium near 400°C (752°F). Two other methods of obtaining uranium in special form are worth noting. The van Arkel-deBoer method involves thermal decomposition of a halide usually iodide on a hot filament and has been applied to other refractory metals. This method has been applied to the preparation of high purity uranium. When fine uranium powder is needed the reversible decomposition of  $UH_3$  is a convenient source. Reduction of oxide by calcium or magnesium may be used to obtain nonpyrophoric powder directly.

## PHYSICAL PROPERTIES

The physical properties of uranium are summarized in Tables 6 to 9. The sensitivity of these properties to purity and metallurgical history accounts in part for discrepancies between values reported by different workers. The anisotropy of uranium always has to be borne in mind. The values listed here are based on the critical evaluations by Holden and Klein. References to the original work may be found in these compilations, which also include graphical representation and more detailed tabulation of those properties as a function of temperature. These compilations have also provided the information in the next section on mechanical behaviour.

# LITHIUM

## INTRODUCTION

Like a number of rare elements lithium achieved recognition of its potential importance beginning with World War I at which time Germany used lithium metal for two principal purposes (1) hardened lead alloy

B Metal for railway bearings as a substitute for lead tin antimony alloys and (2) light strong aluminium alloys Scleron in which zinc was largely substituted for copper.

In World War II interest in lithium grew rapidly for the United States defense developments. Major uses projected for lithium and its compounds in 1954 were as follows

Anhydrous lithium hydroxide for carbon dioxide absorption.

Lithium chloride for dry batteries.

Lithium hydride for hydrogen generation for air sea rescue equipment.

Lithium hydride as a reagent to produce borohydrides for jet propulsion uses.

Lithium metal for new alloys such as the magnesium lithium alloys.

Lithium metal lithium aluminium hydride and lithium amide for organic syntheses.

Now in 1960 the major projected uses for lithium appear to be in the following areas.

Lithium hydride as a reagent to produce borohydrides for jet propulsion uses.

Lithium perchlorate as an oxidizer for solid propellant rockets.

Lithium metal for new alloys such as magnesium lithium and aluminium lithium alloys.

Lithium alkyls as stereospecific polymerization catalysts.

Lithium metal lithium aluminium hydride and lithium amide for organic syntheses.

Lithium 6 in atomic energy.

Lithium fluoride as a cell additive in the electrolytic production of aluminium.

It must be recognized that lithium compounds had been used for over a century before the World Wars for ceramics and medicinals and for some years in the Edison alkaline storage battery.

The element lithium was discovered by Arfvedsen in Sweden in 1807 during his examination of specimens of the mineral petalite a lithium aluminium silicate. This discovery was followed by the researches of many scientists notably Sir Humphry Davy Gmelin Berzelius Bunsen and Matthiesen.

Lithium is element 3 in the periodic system only hydrogen and helium preceding it. It is the lightest metallic element. It has two isotopes lithium 6 and lithium 7 with an atomic weight of 6.94 indicating a predominance of lithium 7.

## OCCURRENCE

Lithium is found widely distributed in the earth's crust calculated to be approximately 0.004 per cent. By way of comparison 0.002 per cent represents the occurrence of lead and 0.0006 the occurrence of tin. Lithium occurs as a silicate phosphate fluoride and chloride. The silicate minerals provide the main commercial source of lithium raw material.

Notwithstanding the relatively high quantity of lithium in the earth's crust actual deposits of sufficient concentration and quantity to warrant commercial mining and recovery operations are limited.

Lithium minerals are found in some quantities on all the continental land masses. From all data available the occurrences would be in the following order of commercial importance North America Africa South America Europe Australia Asia.

If dependent solely on the recovery of high grade minerals a lithium industry of any magnitude could not be developed. In earlier years the Etta mine in the Black Hills South Dakota yielded large quantities of spodumene of high quality but in that period the demand for lithium products was quite limited. Desert lake brines in California yield substantial quantities of lithium as a phosphate ( $\text{Li}_2\text{NaPO}_4$ ) but only as a by product of potash and borax production.

The principal lithium minerals useful for commercial recovery are as follows

Spodumene  $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  containing approximately 8.0 per cent  $\text{Li}_2\text{O}$ .

Lepidolite lithium mica  $\text{R}_3\text{Al}(\text{SiO}_2)_3 (+\text{F})$  containing 3 to 5 per cent  $\text{Li}_2\text{O}$ .

Amblygonite  $\text{LiAlFPO}_4$  containing 8 to 10 per cent  $\text{Li}_2\text{O}$ .

Petalite a lithium aluminium silicate containing 2 to 4 per cent  $\text{Li}_2\text{O}$ .

Desert lake brines containing lithium sodium phosphate ( $\text{Li}_2\text{NaPO}_4$ ).

Lithium minerals are usually found in pegmatite dikes which must be of sufficient width to justify mass mining operations. Depth of such mineralization increases with the length of the dikes. Depths usually vary from 200 to 500 ft in some cases to 1 000 ft. The lithium content of these dikes useful for commercial mining operations is usually from 1 to 2 per cent lithium oxide.

Lithium minerals were usually recovered by hand picking. As the demand increased mass mining methods were introduced and the mineral concentrates were produced by two methods (1) froth flotation and (2) heavy media sink float (magnetic reagent). Froth flotation appears to be the most satisfactory method to produce concentrates containing 4 to per cent  $\text{Li}_2\text{O}$ .

### Cost Considerations

As in other metallurgical products the cost of lithium metal is largely dependent on the cost of raw material. A minimum size of mine flotation mill for economic recovery of lithium is 150 to 200 tons raw material/24 hr producing 30 to 40 tons of 4 to 6 per cent concentrates. In 1946 such concentrates could be produced for \$4/unit of lithium oxide at the mines. In 1952 these costs were of the order of \$7/unit of lithium oxide which is equivalent to 17.5 cents/lb of lithium carbonate recovered (80 per cent recovery). To produce 1 000 lb of lithium metal a minimum of 6 250 lb of lithium chloride is required. To produce this amount of lithium chloride 5 700 lb of lithium carbonate are used or 2 280 lb of lithium oxide. If extraction recovery is maintained at 90 per cent then approximately 25 tons of raw material concentrates containing 5 per cent lithium oxide would be required. Therefore the raw material cost per 1 000 lb of lithium metal would be as shown above.

Allowing for the cost of extraction salt conversion and electrolysis to produce metal and also for capital costs overhead and profit the price of lithium metal in quantities of 100 000 lb/annum or more will be approximately 10 to 15 times the raw material cost.

Capital costs including working capital will be of the order of \$5 to \$8/lb/annum production including all operations from extraction to metal production.

### CONVERSION OF ORES TO LITHIUM CHEMICALS

Having obtained ore concentrates the problem of extracting and recovering lithium becomes all important.

Methods tried and utilized are as follows

Heating with potassium bisulfate and then leaching out lithium sulfate.

Using spodumene to furnish alumina and silica to produce portland cement. Spodumene is added to limestone and calcium chloride. The entire mixture is calcined in a kiln to produce cement clinker and the lithium is volatilized as an impure chloride.

Heating spodumene concentrates at  $1000^\circ\text{C}+$  ( $1832^\circ\text{F}$ ) (below fusion) to convert from alpha phase to beta phase spodumene. The material is cooled and finely ground incorporated with sulfuric acid and heated to approximately  $300^\circ\text{C}$  ( $572^\circ\text{F}$ ) then cooled and leached to produce an impure solution of lithium sulfate.

Heating spodumene ore at  $1038^\circ\text{C}$  ( $1900^\circ\text{F}$ ) or lepidolite ore at  $871^\circ\text{C}$  ( $1600^\circ\text{F}$ ) with 3 parts of ground limestone in a rotary kiln. The sinter is leached with water to give lithium hydroxide monohydrate.

The First method was utilized in Germany but did not give maximum yields or lowest costs. It was primarily a batch process.

The second method affords an interesting means of extracting lithium as a by product provided it is carried out on a large scale wherein portland cement can be commercially produced at least 1 000 bbl/24 hr.

Ninety eight per cent of the lithium can be volatilized but the subsequent purification of the condensed lithium chloride presents very difficult problems.

The third method offers a continuous process with good economy whereby at least 90 per cent of the

contained lithium can be recovered. The sulfate solution is easily filtered to remove the aluminium silicate residue purified of minor impurities and recovered as quite pure lithium carbonate. Soda ash ( $\text{Na}_2\text{CO}_3$ ) is added to the sulfate solution precipitating insoluble lithium carbonate with Glauber's salt ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) as a by product.

The fourth method offers recovery percentages lower than the third method. When treating spodumene the inversion step is not necessary.

Table 1. summarizes the processing operations of the various United States producers of lithium compounds. The third method described above is the Lithium Corp. of America process and the fourth method is that practiced by American Lithium Chemicals and Foote Mineral Company.

With pure lithium carbonate or hydroxide as a starting chemical all of the useful lithium compounds can be produced advantageously.

Other methods of extraction and recovery have been considered among them the volatilization of lithium compound from electric furnace reductions. Lithium minerals and compounds are excellent fluxes but as such are quite costly necessitating very complete volatilization and recovery of the lithium or absorption in slag with subsequent costly method of extraction and recovery.

### Production of Lithium Metal by Fused Salt Electrolysis

In this chapter attention is focused primarily on lithium metal. Various methods have been proposed to reduce lithium compounds to metal but results are costly as compared to the classical method. Lithium chloride admixed with potassium chloride is fused. Current is applied depositing lithium metal on the cathode and evolving chlorine at the anode. In many respects the technology is comparable to the electrolytic reduction of magnesium chloride. Some typical operating data for commercial cells are given in Table 2.

Unit cell capacity is relatively small 80 to 100 lb of lithium metal/24 hr. When demand would justify it cell capacities may be increased advantageously to possibly 500 lb 24 hr. For large scale production cells may be operated in series to permit the use of standard electrical equipment generating 125 to 250 volts d c.

Using salts approximating a eutectic mixture the temperature of the molten bath can be maintained at a minimum  $450\text{--}500^\circ\text{C}$  ( $842\text{--}932^\circ\text{F}$ ) (LiCl 60 per cent KCl 40 per cent approximately). Deterioration of the graphite anodes is thereby minimized.

Lithium metal thus produced will contain certain impurities principally sodium. Practically all of the sodium present in the lithium chloride is deposited with and remains in the lithium metal produced.

## BERYLLIUM

### INTRODUCTION

In 1797 Vauquelin discovered the element beryllium as a constituent of the mineral beryl. In the French language the element is referred to as glucinium (Gl). This name is derived from the sweetish taste of many of its compounds.

The first metallic beryllium was produced by Wohler and Bussy in 1828. They obtained beryllium in the form of an impure powder by reducing beryllium chloride with metallic potassium.

During the nineteenth century numerous other investigators contributed to the development of the chemistry of beryllium. Of particular interest is the work of the French scientist Lebeau published in 1899 which includes descriptions of the electrolysis of sodium beryllium fluoride resulting in the production of small hexagonal beryllium crystals and the preparation of beryllium copper alloys by direct reduction of beryllium oxide with carbon in the presence of copper. Also of interest is the work by the German scientist Oesterheld who in 1916 published the equilibrium diagrams of beryllium with copper aluminium silver

and iron and the investigations by Wilhelm Kroll W. B. Donahue and C. Adomali who all worked on methods of producing pure beryllium by reducing mixtures of beryllium fluoride and alkaline earth and alkali fluorides with alkaline earth metals and magnesium.

Commercial development of beryllium in the United States was begun in 1916 by Hugh S. Cooper who produced the first significant beryllium metal ingot and by the Brush Laboratories Company which started their development work under the direction of C. B. Sawyer in the early 1920 s. In Germany the Siemens Hakke Konzern began their commercial development work in 1923.

Beryllium alloys made their commercial appearance in the United States in 1932 when the American Brass Company using beryllium copper master alloy produced by the Beryllium Corporation of America made available the first rolled beryllium copper. The developments of the Brush Laboratories Company were taken over by the Brush Beryllium Company in 1931. This company entered the beryllium copper field in the early 1930 s and was the first company to develop a commercial process to produce and market metallic beryllium in solid form.

Beryllium is the first element in Group II of the periodic system of elements. Its atomic number is 4 its atomic weight 9.013 and it has a valence of two corresponding to 2s electrons in the L shell. No isotopes have been found in beryllium occurring in nature. Radioactive isotopes of mass numbers 6 7 8 10 and 11 however have been artificially produced.

Metallic beryllium is grayish in colour. Large crystals of bright metallic luster are usually discernible. It is a very light metal (specific gravity 1.845) and is known as the only such metal combining good physical strength with a high melting point [1285°C (2345°F)].

## OCCURRENCE

There are some 30 recognized minerals containing beryllium only 3 are of significance viz. beryl ( $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ ) phenacite ( $2\text{BeO} \cdot \text{SiO}_2$ ) and bertrandite ( $4\text{BeO} \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$ ). Of these three only beryl is now of industrial importance. However substantial low grade deposits of the other two minerals have now been found. The recovery of beryllium from these low grade ores is now under investigation. In pure form this mineral is a beryllium aluminium silicate containing approximately 14 per cent beryllium oxide ( $\text{BeO}$ ) 19 per cent aluminium oxide ( $\text{Al}_2\text{O}_3$ ) and 67. per cent silicon dioxide ( $\text{SiO}_2$ ). The pure composition is approached in the precious forms of beryl emerald and aquamarine.

Industrial grades of beryl ore now reaching the market contain approximately 10 to 12 per cent beryllium oxide. Rarely is ore of more than 12 per cent beryllium oxide available and the trend is toward a supply ranging from 11 percent downward to the marginal ores containing less than 9 per cent. Other constituents of the ore are aluminium oxide 17 to 9 per cent silicon dioxide 64 to 70 per cent alkali metal oxides 1 to 2 per cent iron 1 to 2 per cent and minor amounts of other oxides. Feldspar quartz and mica are the principal mineral contaminants of commercial grades of beryl ore.

Occurrences of beryllium in the earth's crust are widely distributed and are estimated to amount to approximately 0.001 per cent. Beryl ore containing 10 to 12 per cent beryllium oxide however has not as yet with one or two exceptions been found anywhere concentrated in large enough quantities to be mined economically for its own sake. The supply is therefore generally obtained as a by product of mining feldspar lithium or mica in pegmatite dikes and only those crystals which are large enough to be hand sorted and cobbled are recovered. The best producing pegmatites suitable for hand sorting and cobbing contain 1 to 2 per cent beryl ore. The by products from these operations and low grade beryl ore containing about 0.1 per cent beryl will require beneficiation processes to recover the beryl. According to the Bureau of Mines reserves of such low grade ores in the United States amount to over 1 000 000 tons of beryl ore content.

Recently privately owned facilities for concentrating low grade beryl ores have been constructed in

Colorado. The feasibility of operating these mills on an economic basis has not yet been established. The principal producers of beryl ore are the Union of South Africa Argentina Brazil and India. Small amounts are produced in British East Africa French Morocco Mozambique. Portugal and Canada. In the United States the principal sources are found in Colorado Maine New Hampshire and South Dakota. Many undeveloped deposits are located in Canada particularly in the Great Slave Lake area of the Northwest Territories. Most of the beryl ore consumed by the beryllium industry in the United States is imported. Up to this time the supply of hand sorted and cobbled ore has been more than sufficient to meet the industrial demand.

## PRODUCTION

### Pure Beryllium Oxide

The technical grades of beryllium hydroxide or beryllium oxide produced as intermediate products in the production of beryllium metal and beryllium copper master alloy contain as a major impurity salts of sodium and also minor amounts of elements occurring in commercial grades of beryl ore (Si Fe Al Cu Mg Li Mn etc.).

These impurities are generally removed or substantially reduced by dissolving the technical grade hydroxide in sulfuric acid and purifying the formed beryllium sulfate by re crystallization. The pure beryllium sulfate crystals obtained in this manner are then heated in gas fired firebrick furnaces to drive off sulfur trioxide (as SO<sub>2</sub>) leaving a pure grade of beryllium oxide as a residue. To remove all sulfur in the oxide temperatures of 1000 1200°C (1832 2192°F) are required in a reducing atmosphere.

An extremely pure but very expensive grade of beryllium oxide can also be produced by converting the technical grade beryllium hydroxide into beryllium base acetate [BeO.3Be (C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>]. The impurities remaining in this salt are separated by extracting the basic acetate with chloroform filtering the solution to remove the insoluble impurities evaporating the chloroform and subliming the residue. The pure basic acetate so obtained is subsequently fumed down with chemically pure sulfuric acid. The resulting pure beryllium sulfate is then decomposed as noted above.

### Beryllium Metal

All pure beryllium metal now produced in the United States is made by the reduction of beryllium fluoride with magnesium metal. The beryllium fluoride used is produced from beryllium hydroxide.

In this process developed by Kjellgren and used by The Brush Beryllium Company an excess of beryllium fluoride is used in relation to the amount of magnesium added.

The reaction which is carried out in a graphite lined furnace is kept under control by gradually charging magnesium metal and beryllium fluoride in solid form at a furnace temperature of about 9000C (16520F). The heat generated by the reaction is absorbed as fast as it is liberated and serves to supply part of the heat required to melt the solid magnesium and the beryllium fluoride. Since the reaction is carried out below the melting point of beryllium the metal is produced as very fine particles dispersed in a slag consisting of the magnesium fluoride formed by the reaction and the excess beryllium fluoride used.

The beryllium particles are melted and coalesced by raising the furnace temperature to somewhat above the melting point of beryllium. At this temperature the slag is very liquid because of the presence of the excess beryllium fluoride and the molten beryllium separates well and floats on the molten slag. As soon as this occurs the molten metal and the slag are poured out together into a cold graphite crucible and solidified. In the process of pouring the molten beryllium metal is broken up into pebbles so that the solid mixture obtained in the graphite crucible consists of beryllium pebbles embedded in solid slag. This mixture is broken up and the beryllium pebbles and the excess beryllium fluoride present in the slag are recovered in the process which is used for producing the beryllium fluoride from beryllium oxide.

In this process the beryllium oxide is dissolved in a solution of ammonium hydrogen fluoride. The

ammonium beryllium fluoride solution produced in this manner and the ammonium beryllium fluoride solution recovered from leaching out the excess beryllium fluoride present in the mixture of the pebbles and slag resulting from the reduction are mixed together and treated with lead peroxide calcium carbonate and ammonium polysulfide to precipitate impurities. After filtration extremely pure ammonium beryllium fluoride is recovered from the filtrate by evaporation and crystallization.

In this manner the pure ammonium beryllium fluoride crystals produced in the process are derived both from beryllium oxide the raw material and from the beryllium fluoride present in the recycled slag.

The crystals obtained are then decomposed by heat into ammonium fluoride vapour which is absorbed in water and recycled to the step of leaching the beryllium fluoride containing slag and into molten beryllium fluoride which is collected in the form of small clear droplets or lumps.

After leaching the mixture of pebbles and slag resulting from the metal reduction step in order to recover the soluble beryllium fluoride the beryllium pebbles are easily separated from the remaining insoluble small crystals of magnesium fluoride.

Beryllium pebbles obtained in this manner are remelted in a beryllium oxide crucible heated in a vacuum furnace.

The purity of the metal is controlled by the purity of the beryllium fluoride and the purity of the magnesium used.

A flow sheet of the Brush Beryllium Company process for recovering beryllium metal from beryllium hydroxide is shown in Figure 3.

Processes for producing beryllium in flake form by electrolysis of molten mixtures of beryllium and alkali chlorides have been worked out by Cooper Sawyer and Kjellgren and Morana. These processes have so far not been used in industrial practice in the United States. Thepechiney Company in France has however over a period of years produced beryllium flake by chloride electrolysis although it is reported that their production is minor in comparison with the production in the United States.

# SELENIUM

## INTRODUCTION

In 1817 John Jacob Berzelius a professor of chemistry in Stockholm and secretary of the Swedish Academy of Science was studying along with J. G. Gahn a method formerly in use at Gripsholm Sweden for the production of sulfuric acid. As a part of this study an examination of the acid itself revealed a sediment which gave forth an offensive odour previously identified by Klaproth as an indicator of the presence of tellurium. J. G. Gahn it appears recalled detecting a similar odour in those plants where the Fahlun copper concentrates were smelted and the resulting sulfur used to produce sulfuric acid. In the hopes of finding a new source of the then rare element tellurium in this acid Berzelius obtained larger quantities of this residue but his work proved to no avail for he could find no trace whatsoever of tellurium. He did notice though as a result of his tests that there remained unaccounted for an unknown substance whose chemical properties closely resembled those of tellurium. So closely akin were these two elements that Berzelius decided to call the former selenium from the Greek word *selene* meaning the moon tellurium having been derived from the Latin word *tellus* meaning the earth.

Although discovered in 1817 selenium remained a laboratory curiosity for some 50 years. Finally in 1873 Willoughby Smith while testing various materials for electrical conductivity discovered quite by accident that the current resistance of this element decreased as the intensity of illumination increased and furthermore that resistance increased slightly as the temperature likewise increased above 170°C (338°F). This led among other things to the development of the photoelectric cell of which more will be said later on but the important fact is that for the first time it brought selenium into the public eye. Once there a

multitude of applications developed until now plays a very definite part in our everyday life.

## OCCURRENCE

Selenium the fortieth element in plentifulness falling between bismuth and gold rarely occurs in its native state. Although occasionally found in conjunction with native sulfur and in the form of selenides of other metals in such minerals as clausthalite  $PbSe$  eucaisite  $CuAgSe$  crookesite  $(CuTIAg)_2Sc$  naumannite  $Ag_2Se$  and zorgite  $PbCuSe(?)$  it is most frequently found as an accessory mineral in base metal ores of lead copper and nickel. Whenever any of the above are treated selenium is recoverable as a by product. The main sources of selenium in this country originate in the copper mining states of Utah Arizona and New Mexico the Montana ores running low in this element. Selenium from these sources and from Mexican copper mined in the states of Durango and Zacatecas is recovered by the American Smelting and Refining Company Anaconda Copper Mining Company the American Metal Climax Company and recently Kennecott Copper Corporation in this country. In Canada the International Nickel Company of Canada Ltd. recovers selenium from the Sudbury copper nickel ores and the Canadian Copper Refiners Ltd. of Montreal from the copper anodes derived from the copper zinc ores of Flin Flom Manitoba. In Australia selenium is produced by the Electrolytic Refining and Smelting Company Pty. Ltd. in Sweden by the Boliden Mining Company in Belgium by the Societe General of Hoboken in Japan by the Taihi Besshi and Nippon mining companies and in the Western Zone of Germany by the Norddeutsche Affinerie of Hamburg. Prior to World War II selenium was produced in what is known as the East Zone of Germany but that source along with all other production in the U.S.S.R. and other Soviet dominated countries behind the Iron Curtain has become an unknown factor today.

## DERIVATION

Many years ago the sole source of selenium was thought to be from the flue dusts of metallurgical processes utilizing sulfide ores however recovery from this source is virtually nonexistent today and the anode muds or slimes from electrolytic copper refineries provide the source of most of the world's selenium. Basically there would appear to be three main methods of recovering selenium by roasting with soda by roasting with sulfuric acid and by smelting with soda and niter variations of these are found to accommodate the variances in basic raw materials being handled.

In the first method that of roasting with soda the decopperized slimes are mixed with soda and raised to temperatures well below the sintering point with sufficient air to oxidize the selenium. The selenium is recovered as sodium selenate from the water leached calcine by evaporation. The sodium selenate is reduced to the selenide by coke then redissolved and blown with air and the selenium is precipitated with sulfur dioxide the sodium hydroxide being carbonated and recirculated.

In the sulfuric acid roasting the raw slimes are treated with sulfuric acid prior to roasting. During the course of roasting the selenium dioxide is driven off and collected in a wet scrubber Cottrell system. The remainder of the selenium is largely recovered by the conventional soda smelting process.

The soda smelting process is a pyrometallurgical one in which the decopperized slimes are mixed with soda and silica. After the first slags are drawn off the molten charge is rabbled with air and some of the selenium is volatilized and caught in a scrubber Cottrell system. To the charge is now added caustic and niter. The slag which results high in both selenium and tellurium is crushed and leached with water to which is added fresh sulfuric acid to precipitate the tellurium. The solution is then treated with sulfur dioxide to precipitate the selenium.

There are at present in the United States and Canada seven producers of this element with a total output of between 1 and 1.4 million pounds annually. Stimulated by the Korean conflict increased demand for selenium especially for rectifier manufacture starting in 1951 led to an acute shortage for this element. Material improvements in recoveries by selenium producers resulted in increased production ending the

shortage by the fall of 1956 At present and for the foreseeable future the supply of selenium should be adequate to take care of any reasonable demand based both on production potential and stocks in the hands of producers.

Pricewise selenium can hardly be termed an inexpensive commodity at \$7.00/lb retail in its commercial form as quoted by domestic producers. This price for domestic material has ranged from a low in the early 1930 s of \$1.50/lb to a high of \$15.50/lb in 1956.

## PHYSICAL PROPERTIES

Selenium atomic number 34 is the third member of Group VI of the periodic arrangement of elements.

Selenium is more metallic than sulfur but less metallic than tellurium the two next of kin in the group.

Selenium can be caused to exist as a solid as a liquid or as a vapour at temperatures easily handled in any metallurgical laboratory.

**Amorphous Selenium.** Amorphous selenium occurs as red powder vitreous and colloidal selenium.

**Red Powder.** The amorphous red powder results when solutions of selenous acid of pH 7 to pH 3 and even more acidic with such acids as hydrochloric or sulfuric are treated with strong reducing agents such as sulfur dioxide hydrazine or hydroxylamine hydrochloride. The red powder turns black on standing and on heating yields the hexagonal form.

**VITREOUS.** Vitreous selenium a black mass prepared by quench cooling liquid selenium is glassy and brittle showing conchoidal fractures and is described as a supercooled liquid. It is a dielectric being electrified by friction.

As little as 0.0003 per cent by weight of tellurium in the selenium will increase the plasticity. Vitreous selenium containing 1 per cent of chlorine is quite plastic when first quench cast but within 24 hr even at room temperature it will show substantial conversion to the hexagonal state.

By reflected light glassy (vitreous) selenium is mirror black. Thin layers by transmitted light (daylight) appear blood red. Vitreous selenium is about as hard as glass is perhaps more brittle and shows a pronounced conchoidal fracture. Vitreous selenium is a very poor conductor of heat but if stored in a warm place gradually crystallizes to the hexagonal state which is a better conductor of both heat and electricity. Except for semiconductor use especially xerographic plates vitreous selenium as such may be considered an electrical insulator.

**COLLOIDAL.** Colloidal selenium is prepared by the reduction of dilute aqueous solutions of soluble selenium with such reducing agents as sulfur dioxide hydraline hydrate dextrose or titanium trichloride. It can also be prepared by pouring a solution of selenium in carbon disulfide into a large volume of ether and by passing an electric current through a solution of selenous acid between a platinum anode and a selenium coated cathode.

The colours obtained vary from violet to red depending on the conditions during precipitation.

**Crystalline Selenium.** Crystalline selenium occurs as either monoclinic or hexagonal forms.

**MONOCLINIC.** Monoclinic selenium is obtained by the low temperature evaporation of carbon disulfide containing dissolved selenium. Heat and several other conditions convert the mono clinic selenium to the hexagonal state.

**HEXAGONAL.** Hexagonal selenium is considered the most stable state of selenium under ordinary conditions. It has a gray metallic appearance is a fair conductor of heat and electricity is fairly inert to atmospheric conditions has fair mechanical strength and is easy to produce by heating any form of selenium until crystallization is complete.

### The Liquid State

The melting point of hexagonal selenium is 217°C (423°F) and represents a definite transition from solid to liquid. Amorphous selenium begins to soften at about 1000C (2120F) and its behaviour at increasing

temperatures depends on the rate of heating. It liquefies at 2170C (4230F).

Molten pure selenium no water from what allotrope it is obtained is not very fluid until heated several dozen degrees above the melting point of 2170C (4230F).

Unlike sulfur selenium becomes more fluid with increasing temperature. Liquid selenium can be boiled at atmospheric pressure [684.90C (12650F)] in a porcelain dish or in a quartz dish without bumping. Liquid selenium probably contains several molecular species.

# THE PLATINUM METALS

## INTRODUCTION

The first known reference to platina or native platinum a naturally occurring alloy composed of a large proportion of platinum together with palladium rhodium iridium osmium ruthenium copper iron and sometimes gold bears the date 1557. The writer was Julius Caesar Scalinger (or della Scalla) an Italian poet and scholar who noted the difficulty in melting a metal which was obtained from the Spanish possessions in South and Central America. The earliest scientific investigation of platina was instigated by William Brownrigg in 1750. Berthollet and Pelletier described the work of M. de l'Isle who obtained a malleable form of platinum in 1773-74. Pierre Francois Chebaneau (or Chavaneau) succeeded in preparing some malleable platinum and patented the process in 1783. However an intensive study of the records has led to the belief that pure platinum was first obtained in 1803 by W. H. Wollaston whose brilliant researches resulted in the isolation of two of the minor constituents of platina i.e. palladium and rhodium. The aqua regia extract of platina was treated with ammonium chloride to precipitate the platinum mercury (I) cyanide was then added to precipitate the palladium and finally rhodium was isolated as sodium rhodium chloride.

The name palladium was chosen by Wollaston in honor of the asteroid Pallas and rhodium because of the rose red colour of the salts of that metal. Osmium and iridium were isolated and named in 1804 by S. Tennant. About the same time H. V. Collet Descotils A. F. de Fourcroy and L. M. Vauquelin also suspected the presence of iridium in platina but their work was not conclusive. Both osmium and iridium were found in the black residue which remained after the aqua regia treatment of platina. The name iridium was derived from the Greek word *iris* meaning a rainbow and refers to the varying colours of iridium salts. The name osmium derived from the Greek word for smell or odour was chosen because of the characteristic chlorine like odour of osmium tetroxide. It was not until 40 years later that the remaining element of the platinum group was isolated. Ruthenium was discovered and named by C. Claus in 1844. although publication of the news was delayed until the following year when J. J. Berzelius confirmed the results of the experiments and accepted ruthenium as a new element. The name ruthenium from Ruthenia Russia was first used by G. Osann in 1828 to designate a substance obtained from platina this substance was later shown to be composed of the oxides of silicon zirconium titanium iron and a small quantity of a new element.

## OCCURRENCE

The platinum metals occur both in primary deposits and in placers. The primary deposits are of two main types. The first consists of disseminations or local concentrations of the metals in olivine rich rocks particularly in dunite and often associated with chromite native platinum or iridosmine is the principal constituent. The erosion of such deposits has been responsible for the formation of placer deposits of the platinum metals. Dunite deposits are widespread the most important commercially being in the Ural Mountains region of the U.S.S.R. and at Overwacht in the Transvaal Union of South Africa. The second type of primary deposit includes the magmatic nickel copper sulfide deposits which are generally associated with norite. These deposits in which platinum and palladium predominate make up the greatest

known reserves of platinum metals. The most extensive deposits have been found in the norite belt of the Bushveld igneous complex in the Transvaal and in the Sudbury district of Ontario Canada. In the Sudbury district ores platinum and palladium occur in about the same proportions these ores also contain small amounts of the other platinum metals as well as silver and gold. The precious metals are obtained as by products during the extraction of nickel and copper. The South African primary deposits contain all the platinum group metals as well as iron nickel copper cobalt silver and gold. In contrast to the Ontario ores the quantity of base metals present is not sufficient to pay for the working costs. Platinum metals have also been found in quartz veins and in copper and coal deposits although these sources are of little economic value.

Placer or alluvial deposits of great economic importance have been found in the Permian district of the Ural Mountains in Colombia South America and in Abyssinia. Placers have also been found in the United States including Alaska Australia and Canada.

Very few compounds of the platinum metals occur as minerals. Sperrylite ( $\text{PtAs}_2$  with which small amounts of rhodium are sometimes associated) occurs in the Sudbury district in Canada in the Transvaal deposits of South Africa and in eastern Siberia. Cooperite ( $\text{PtS}$ ) and braggite ( $\text{Pt Pd Ni}_3\text{S}$ ) are found in the Bushveld complex and in the Potgietersrust districts of the Transvaal. Of the minerals which contain palladium principally stibiopalladinite ( $\text{Pd}_3\text{Sb}$ ) is found with sperrylite in the Transvaal and potarite ( $\text{PdHg}$ ) is found only in British Guiana. Laurite ( $\text{RuS}_2$ ) which sometimes contains osmium is very rare it is found in Borneo and in the Transvaal.

Iridium is most often found alloyed with osmium in iridosmine ( $\text{Ir} > \text{Os}$ ) and siserskite ( $\text{Os} > \text{Ir}$ ). The term *osmiridium* is used more or less synonymously with the term *iridosmine* but the latter is employed in this chapter. Iridium is also associated with platinum and gold in platiniridium and aurosmiridium respectively. As mentioned previously rhodium together with other members of the platinum group occurs as a minor constituent of native platinum the proportion of rhodium is usually less than 1 per cent. Small quantities of ruthenium are associated with alloys of the platinum metals but most frequently with iridosmines which may yield 12 per cent or more of ruthenium. It must be noted however that some types of iridosmines are very resistant to corrosion and as a result the analysis errors may be large.

## PRODUCTION AND ECONOMIC STATISTICS

In the first edition of this handbook the authors included estimates of world production of crude platinum up to the end of 1916 and of average annual outputs by countries from 1921 to 1952. This information is largely of historical interest and has not been retained for this edition. It is perhaps interesting to note that in the period from 1950 to 1957 world production of the platinum metals doubled. This increase is mainly the result of a greater than fourfold expansion in the South African production this country's output now accounts for more than half of the estimated world production. In the same period Canadian output increased by approximately 50 per cent while that of the U.S.S.R. is estimated to have increased by 25 per cent. In 1958 a drop of about 30 per cent in world production was reported.

Notwithstanding the record production of these metals in 1957 figures for world consumption showed a decrease from the previous year and a further decrease of about 20 per cent was estimated for 1958. This has been attributed mainly to a reduction in demand from the petroleum industry in the United States but undoubtedly it is related to the period of economic recession in North America in 1957-58 which saw a decline in consumption of many base metals as well. In 1959 industrial demand increased and in consequence there was a limited increase in production in both South Africa and Canada.

It is significant that increased production and decreased consumption brought the prices of these metals down appreciably below the figures for the previous 6 years. In fact the price of platinum for January 1 1959 was as low as at any time since World War II. With the resumption of demand in 1959 there has been

a slight upward turn in prices although these remain lower than the average of the previous five years.

## DERIVATION

The methods by which platinum metals are obtained from their naturally occurring sources and from scrap precious metals should be discussed under various headings according to the source of the raw material. It may be advisable to point out that by tradition refiners of the platinum metals have long been reluctant to disclose the details of their operations accordingly the descriptions that follow which are based on published material only may depart in detail from prevailing practice.

### Extraction of Platinum Metals from

#### Canadian Nickel Ores

As has been mentioned earlier in this chapter platinum metals occur associated with the copper nickel sulfide ores in the Sudbury district of Ontario. The total content of platinum metals is only of the order of  $\frac{1}{2}$  ppm but in view of the large tonnages of nickel produced (Figure 1. Process Flow chart for the recovery and separation of platinum metals. First stage ore to platinum concentrates the quantities of platinum metals made available are sufficient to make this an important source. The bulk of the nickel refining in the Sudbury basin is carried out by the International Nickel Co. a smaller proportion being mined by the Falconbridge Nickel Co. Expansion of the production of the former company includes a new project in the Mystery Lake Moak Lake district of northern Manitoba about 400 miles north of Winnipeg. Present indications are that this ore body will also produce platinum metals as by-products and that this known as the Thompson Mine will become the second ranking producer of platinum metals in Canada. Production is expected to begin in 1960 or 1961. The manner of obtaining the platinum metals from these ores is obviously integrated with the processes employed for the isolation and refining of nickel and copper. These are described in recent reference works on production metallurgy. The essential stages in the operations of the International Nickel Co. are outlined in Figure 1. The bulk of the platinum metals is separated from the nickel and copper during slow cooling of the Bessemer matte. During the preparation of this the amount of oxidation of sulfur is controlled to produce a small amount of metallic nickel and copper which acts as a collector to separate the platinum metals from the metallic sulfides. This precious metal alloy is magnetic and may be removed by passing the ground matte through a magnetic separator. This product is melted and treated with enough sulfur to convert 80 to 90 per cent of the nickel and copper to sulfides at the same time retaining a small proportion of these metals in the free state. On cooling this matte a still more concentrated metallic alloy containing the platinum metals separates and is removed from the ground material magnetically. This enriched alloy can then be subjected to electrolytic refining during which the platinum metals accumulate in the anode slimes.

Falconbridge Nickel Mines Ltd. separate a rich concentrate by magnetic cobbing then subject the remainder to flotation and a further wet magnetic separation. The concentrate is smelted in a blast furnace to give a matte which is further upgraded by treatment in basic lined converters to yield a high grade shipping matte. This matte containing about 48 per cent nickel 28 per cent copper and 22 per cent sulfur is shipped to the company's subsidiary refinery at Kristiansand in the south of Norway for further treatment. There it is roasted the copper removed from the calcine by acid leaching and the nickel recovered by electrolysis. The anode slimes from this electrolysis are smelted and re-electrolyzed to give a concentrate of precious metals which is refined in the same plant in Norway. The operations of this company have been described in detail in a recent publication.

## TANTALUM

Tantalum atomic number 73 atomic weight 180.95 is located in Group VB of the periodic table below its sister element columbium and adjoined by hafnium on the left and tungsten on the right.

It is a strong ductile metal characterized by (1) its high density 16.6 g/cc (2) its high melting point 2996°C (5425°F) the third highest among the metals exceeded only by rhenium. 3180°C (5756°F) and tungsten. 3410°C (6170°F) (3) the tenacious thin oxide layer on its surface which gives it superior rectifying and capacitance properties and (4) its extreme inertness to attack by all acids except hydrofluoric and fuming sulfuric at ordinary temperatures.

## History

Tantalum was discovered in 1802 by Ekeberg of Sweden he named it after Tantalus in Greek mythology because of the difficulty of dissolving the oxide. In 1801 Hatchett of England had announced the discovery of columbium because of the similarity of the properties of the compounds of those two elements for over forty years the two were regarded as identical although Wollaston suspected their dissimilarity. In 1844 H. Rose a German chemist made exhaustive studies of the columbite of Bodenmais and showed that this mineral contained two metallic acids one of tantalum and the other of what he supposed to be a new metal which he named niobium (for Niobe the daughter of Tantalus).

According to the distinguished American chemist J. Lawrence Smith in a note published in 1877 Rose believed in 1844 that the tantalum of this mineral was the same as what was equally well known as columbium. Thus it appears that he regarded the other metal in the mineral as a new element and did not simply apply another name to Hatchett's columbium. Subsequent examination however convinced Rose that the two metallic acids obtained from the Bodenmais columbite were really the original columbic acid of Hatchett discovered in 1801 and the tantalic acid discovered by Ekeberg in 1802. In the face of this it is not understood why Rose's new name niobium was accepted then as well as in more recent years in place of Hatchett's original and valid name columbium.

In 1866 Marignac developed his classical method of separating the two sister elements utilizing the difference in the solubilities of their complex potassium fluorides. This permitted studies of the compounds of each element.

None of the early investigators actually isolated anything more than an impure form of either metal. The first ductile tantalum was produced by W. von Bolton in 1903 in the Siemens Halske plant in Berlin. It was the first metallic filament for incandescent lamps and approximately 11 million tantalum lamps were made before tungsten began to replace tantalum for this application in 1909.

Tantalum was first produced in the United States in 1922 by C. W. Balke and commercial production has continued since that time. It is interesting to note that one of Balke's motives in making tantalum was to take advantage of its chemical inertness and use it as an anode in the corrosive chlorine cell electrolyte. He soon discovered that an oxide film of Ta<sub>2</sub>O<sub>5</sub> prevented the flow of current when tantalum was connected as an anode in solutions. This film however makes tantalum an excellent electrolytic valve for use in the rectification of alternating current and the first large commercial application of the metal was in the Balkite battery charger used extensively in the radio receiving sets of the 1920's.

## Occurrence and Sources

Tantalum ranks fifty fourth in order of concentration of elements in the earth's crust and is definitely an uncommon metal. It is always found associated with columbium which is about eleven times as prevalent. The most important mineral source is a ferrous manganese tantalate columbate (Fe Mn)(Ta Cb)<sub>2</sub>O<sub>6</sub>. If the Ta<sub>2</sub>O<sub>5</sub> content exceeds the Cb<sub>2</sub>O<sub>5</sub> content the mineral is called tantalite if the reverse is true it is called columbite. These minerals are usually found in pegmatite dikes in quantities which seldom exceed a few pounds per ton.

Tantalum is also present in other minerals such as pyrochlore fergusonite samarskite euxenite and pyroterase. In most of these the columbium content exceeds that of tantalum. As the demand for columbium grows the processing of high columbium low tantalum ores should make available increasing amounts of

tantalum concentrates from these sources. In fact a good deal of the tantalum has been and continues to be derived from concentrates higher in columbium than tantalum because of the relative scarcity of tantalum concentrates.

Tantalite has been produced chiefly in western Australia where it was mined from alluvial deposits in the Pilbarra District (now a minor source) in eastern Brazil Nigeria and the Belgian Congo Tantalum concentrates are being produced as by products of tin (cassiterite) placer mining operations in the Belgian Congo and to a minor extent in Malaya. Currently concentrates of this type from the Belgian Congo account for one third of the United States imports of tantalite concentrates.

The United States has only minor and scattered deposits of tantalite tantalum ore mining is almost entirely a foreign industry. More than 99 per cent of the United States tantalite supply is imported. In 1958 some 84 per cent of the imports came from the Eastern Hemisphere. This dependence on water borne ore imports is one factor opposing the greater use of tantalum.

The ores are concentrated by hand separation washing tabling and electrostatic and electromagnetic means. The concentrates as received ordinarily contain 60 per cent or more of combined oxides ( $Ta_2O_5$  and  $Cb_2O_5$ ) and associated impurities are iron tin titanium zirconium silica and manganese. In the concentrates imported into this country the ratio of  $Ta_2O_5$  to  $Cb_2O_5$  varies from 12/1 to 3/4 with the average probably about 1/1 for the bulk of the material.

### Production and Price Statistics

Data on the domestic shipments of columbium tantalum concentrates imports of concentrates ore consumption. It will be noted that the quantities of metal produced are much less than the quantities contained in the ores consumed. This is because the greater portion of both columbium and tantalum concentrates is fed directly to electric furnaces to produce ferrocolumbium and ferrotantalum columbium. These alloys are used in some austenitic stainless steels where about one per cent columbium and tantalum acts to prevent carbide precipitation.

While prices for imported tantalite are not quoted publicly material containing approximately 60 per cent  $Ta_2O_5$  sold in 1959 for 83.50 4.25 per pound of contained tantalum pentoxide. This represented a decline from the prices in the neighbourhood of 86.25/lb at the beginning of 1958.

Prices for tantalum metal have been decreasing in recent years as the number of producers and the total plant production capacity have increased. As of late 1960 tantalum powder was generally available at about \$40 per pound wetting stock at \$35 per pound and sheet at \$55 60 per pound.

### Extraction

In addition to the usual problems encountered in separating a desired metal from the other components of a given raw material the extraction of tantalum from ores or concentrates is even more difficult because of the presence of its chemically similar sister metal columbium. In this respect tantalum and columbium are quite like zirconium and hafnium insofar as the problem of complete separation of the two is concerned.

**Fractional Crystallization.** The classical separation method of Marignac in use since the early 1920 s has been almost completely superseded by solvent extraction methods in recent years. The fractional crystallization process as practiced industrially consists of these steps

Pulverized (about 200 mesh) tantalum concentrates are fused with sodium hydroxide in a continuous furnace to form crude sodium tantalites and columbates.

Cooled flakes of the fusion mass are leached with hot water and then with hydrochloric acid to remove most of the iron manganese silica tin and titanium impurities. Insoluble tantalalic and columbic acids (hydrated oxides) are formed by this treatment.

The mixed tantalalic and columbic acids are dissolved in hydrofluoric acid and sufficient potassium hydroxide or fluoride or carbonate is added to form a solution of potassium fluo tantalate  $K_2TaF_7$  and potassium

columbium oxyfluoride  $K_2CbOF_5$ .

After the hot solution has been filtered to remove insoluble matter the filtrate is allowed to cool in a crystallizer. Potassium fluotantalate which has a solubility of 7.5 gpl in water at room temperature precipitates from the solution while the  $K_2CbOF_5 \cdot H_2O$  which has a solubility of 91.5 gpl in water remains in solution.

The  $K_2TaF_7$  crystals are separated from the slurry by filtration and dried in a steam heated tray dryer.

Tantalum powder is obtained by electrolysis of fused  $K_2TaF_7$  or by sodium reduction of this salt.

The above steps are primarily batch operations and the fractional crystallization process is better suited to production of pure tantalum than of pure columbium. It is for these and other reasons that this process has been largely abandoned as a commercial process in recent years in favour of the liquid liquid extraction method of extracting and separating tantalum and columbium from ores.

**Liquid Extraction.** The present widely used method of separating tantalum and columbium by liquid extraction grew out of work conducted in the early 1950 s by several investigators chiefly those of the U.S. Bureau of Mines Albany Oregon and the Ames Laboratory of the U.S. Atomic Energy Commission. The basic principles relate to the effect of acid concentration on the relative solubilities of tantalum columbium and other metal fluorides in aqueous and methyl isobutyl ketone systems.

When an acidic aqueous solution of the fluorides of tantalum columbium and the other metals present in the mineral concentrates is placed in contact with methyl isobutyl ketone the tantalum fluoride is extracted by the organic phase at a low acidity and the columbium fluoride at a high acidity. By contrast the other fluorides tend to remain in the aqueous phase. The solubilities are so different that clean extractions of very pure tantalum and very pure columbium can be obtained in a relatively few extraction stages.

In industrial practice the fine ground ore (-200 mesh) is digested with concentrated hydrofluoric acid prepared from anhydrous HF and deionized water in tanks lined with polyethylene or Haveg. The tantalum and columbium oxides dissolve while the bulk of the impurities remains in the gangue. The tantalum columbium liquor is separated from the undissolved solids by filtration and/or decantation and pumped to a holding tank. From here on the processes differ somewhat.

In one plant a stepwise extraction is used. The tantalum columbium feed solution is adjusted to a low acidity and fed to the polyethylene extraction cascade where it is treated with methyl isobutyl ketone in mixers and settlers operating in tandem. The tantalum is first extracted into the organic phase at the low acidity and then stripped from that phase by deionized water to yield an aqueous solution of extremely pure tantalum fluoride. The tantalum free feed solution is acidified to a high acidity with sulfuric or hydrochloric acid and treated with pure methyl isobutyl ketone in the columbium extraction section of the cascade. Here the columbium content is extracted into the organic phase leaving essentially all the remaining dissolved impurities in the aqueous phase. The organic phase is then treated with deionized water to remove columbium fluoride from the ketone as a very pure material in aqueous solution.

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