# Production technologies of CRM from primary

Authors : Dr. Jason YANG (GTK), Xianfeng Hu (MEFOS), Lena Sundqvist (MEFOS), Johan Eriksson (MEFOS), Elina Yli-Rantala (VTT), John Bacher (VTT), Michal Drzazga (IMN), Teodora Retegan (Chalmers)

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| Number of pages | 267 |
| Document type | Deliverable |
| Work Package | WP4 |
| Document number | D4.1 |
| Issued by | GTK |
| Date of completion | 2018-01-31 12:48:29 |
| Dissemination level | Public |

**Summary**

In this deliverable (D4.1) the relevant production lines of CRMs, including production, applications, primary resources for production and main industrial actors, are identified. Flow sheets of mineral and metallurgical processing are analysed and recognized, and further the main challenges related to CRM recovery techniques are discussed. Additionally, the mining tailings and processing residues are characterized.

Approval

| Date | By |
|---|---|
| 2018-01-31 12:57:08 | Mrs. Marjaana KARHU (VTT) |
| 2018-02-14 17:34:55 | Mr. Stéphane BOURG (CEA) |

# Production Technologies of CRM from Primary Resources

**SCRREEN D4.1**

**Jason Yang (GTK)**

*Contributors:*

CHROMIUM, COKING COAL, NATURAL GRAPHITE, MAGNESIUM, SILICON METAL, VANADIUM: Xianfeng Hu, Lena Sundqvist and Johan Eriksson (MEFOS)

GALLIUM: John Bacher (VTT)

NATURAL RUBBER, PHOSPHATE ROCK, PHOSPHORUS: Elina Yli-Rantala (VTT)

BARYTE, PLATINUM-GROUP METALS (PGMs), RARE EARTH ELEMENTS (REE), SCANDIUM, TUNGSTEN: Jason Yang (GTK)

ANTIMONY, COBALT, GERMANIUM, INDIUM: Michał Drzazga (IMN)

BERYLLIUM, BORATES, FLUORSPAR, TANTALUM, BISMUTH, HAFNIUM, HELIUM: Teodora Retegan (Chalmers)

January 2018

CONTENT

# 1  INTRODUCTION

In this deliverable (D4.1) the relevant production lines of CRMs, including production, applications, primary resources for production and main industrial actors, are identified. Flow sheets of mineral and metallurgical processing are analysed and recognized, and further the main challenges related to CRM recovery techniques are identified. Additionally, the mining tailings and processing residues are characterized.

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Xianfeng Hu, Lena Sundqvist and Johan Eriksson (MEFOS): CHROMIUM, COKING COAL, NATURAL GRAPHITE, MAGNESIUM, SILICON METAL, VANADIUM

John Bacher (VTT): GALLIUM

Elina Yli-Rantala (VTT): NATURAL RUBBER, PHOSPHATE ROCK, PHOSPHORUS

Jason Yang (GTK): BARYTE, PLATINUM-GROUP METALS (PGMs), RARE EARTH ELEMENTS (REE), SCANDIUM, TUNGSTEN

Michał Drzazga (IMN): ANTIMONY, COBALT, GERMANIUM, INDIUM

Teodora Retegan (Chalmers): BERYLLIUM, BORATES, FLUORSPAR, TANTALUM, BISMUTH, HAFNIUM, HELIUM

## 2 ANTIMONY

### 2.1 PRODUCTION LINES OF IDENTIFICATION FROM PRIMARY RESOURCES

Antimony (Sb – stibium) is a chemical element of atomic number 51, positioned in the periodic table of elements between metalloids (such as As, Bi – vertically, and Sn, Te – horizontally), and exhibiting similar amphoteric properties. Its properties in metallic state, such as electrical and thermal conductivity and mechanical properties, are rather poor, so as a metal antimony is not use alone. Being hard and brittle and expanding during solidification metallic antimony is used as alloying element in limited group of alloys, where these properties suits to gain specific properties (such as: antimonial lead, babbits and type alloys).

Antimony compounds, such as, especially, diantimony trioxide ($Sb_2O_3$), named widely as ATO, and also antimonates play much more important role in recent technical application fields, being highly valued as catalysts, pigments and components of flame retardants.

Antimony is used mainly in the production of flame retardants as well as battery alloys, sliding bearings, welding agents, electronics and pharmaceuticals. Addition of antimony is increases strength and toughness of metals. Antimony ores may be found mainly in China, Russia and South Africa. Chine itself for the most of the world production accounting for more tan 50% of the global production.

### 2.2 PROCESSING TECHNIQUES RECOGNITION AND ANALYSIS

#### 2.2.1 MINERAL PROCESSING

Antimony is a rare element, with abundance in the Earth crust of 0.2 ppm. In spite of this, it is a component of numerous minerals of an oxidic and especially sulphidic types. The most important antimony minerals present in exploited ore deposits are: stibnite (Sb2S3), berthierite (FeSb2S4), boulangerite (Pb5Sb4O11), stephanite (Ag5SbS4), jamesonite (Pb4FeSb6S14), bournonite (PbCuSbS3), tetrahedrite ((Cu,Fe)12Sb4S13), freibergite ((Ag,Cu,Fe)12(Sb,As)4S13), gudmundite (FeSbS), ullmannite (NiSbS), dyscrasite (Ag3S), breithauptite (NiSb), kermesite (Sb2S2O), valentinite/senarmontite (Sb2O3). Stibnite is the principal source of mined antimony, but- being widely distributed mineral- its economically valuable deposits are not common (e.g. Xikuangshan – China, Murchison – South Africa Rep. [Schwartz-Schampera 2014].

Generally mined antimony bearing deposits contain from 0.1 to 2 wt.% Sb, and antimony is a by-product of gold, silver, lead or zinc sulphidic ores. The presence of precious metals is often a deciding incentive for parallel antimony recovery.

Antimony world reserves are estimated to about 1.5 million metric tonnes and recent mine production- counted at about 130,000 metric tons [USGS, 2017]- is distributed between few countries: China – 100,000 mt., Russia – 9,000 mt, Tajikistan – 8,000 mt, Bolivia – 4,000 mt, Australia (Mandalay) – 3,500 mt, Myanmar – 3,000 mt, Turkey – 2,500 mt, Vietnam – 1,000 and Mexico (US Antimony Corp.) – 1,300 mt, South Africa (Murchison Cons.) – unknown, Canada (Beaver Brook) – suspended activity.

The mineral processing of mined ores is rather tedious activity, comprising: crushing, sorting (including sometimes hand sorting, e.g. at Chineese miners), grinding and physical separation techniques, such as gravity upgrading and flotation, which produce upgraded concentrates with diffent value (from above 5 wt.% Sb to

about 60 wt.%Sb), leaving behind gangues and tailings with Sb content of about 0.2 wt.%, that should be landfilled according to local environmental law.

The list of major world miners comprises among others [Schwartz-Schampera, 2014]:

- Chineese – Hsikwanghan Twinkling Star, Hunan Cheznu Min., China Tin Group, Shenyang Huacheng Antimony;

- Australian – Mandalay Resources

- Russian – GeoProMining

- South African – Murchison Consolidated

- Tajikistanish – Anzob

- Turkish – Cengiz & Ozdemir Antimuan Madenleri.

The produced antimony concentrates are further processed either on site or exported to other processors.

The other primary source for antimony recovery are the by-products from refining of crude lead, recovered from processing of primary copper and lead-zinc concentrates; in this instance the usual route of action is smelting of antimonial lead, with Sb content up to 20%, suitable for manufacturing of different Pb-Sb alloys according to market demand.

## 2.2.2 METALLURGICAL EXTRACTION

### 2.2.2.1 ANTIMONY RECOVERY FROM PRIMARY SOURCES

The upgraded antimony concentrates from primary source (ore mining and mineral processing) contain different Sb concentrations, what determine the methods applied for their processing- either pyrometallurgical of hydrometallurgical.

PYROMETALLURGICAL METHODS

Generally, the concentrates of the lowest grade of sulphidic type (with 5-25% Sb content) are volatilized to raw $Sb_2O_3$; the medium grade (with 25-40% Sb content) are smelted in blast furnace; and – the high grade concentrates (with 45-60% Sb content) are processed by liquation or reduction with iron (so called iron precipitation). These methods are characterized more detailly below [Anderson, 2012, Buttermann, 2004].

Oxide volatilization

Recovery of antimony as volatile $Sb_2O_3$ is the only method suitable for the low grade sulphidic antimonial concentrates, being at the same time almost thermally autogenic process. There are many variants of oxide volatilization supported by the same principles, but realized in different equipment. Sulphur is being burned of at about 1000°C and removed as waste gas, while $Sb_2O_3$ vapours are condensed and collected in gas cleaning system (condenser, Cottrell/precipitator, baghouse). The reactions of roasting and volatilization occur almost simultaneously after heating the charge (concentrate + coke or charcoal) under controlled condition in pyrometallurgical unit, such as shaft furnace, rotary kiln, converter or roaster. This method could be able to

produce high grade Sb2O3 suitable for the use in ceramics and other applications only under special attention of controlling the process conditions. The principal reactions are as follow:

$$2\ Sb_2S_3 + 9\ O_2 \rightarrow 2\ Sb_2O_3 + 6\ SO_2$$

$$2\ Sb + 1.5\ O_2 \rightarrow Sb_2O_3$$
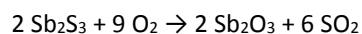
Sulphide liquation

Antimony sulphide could be readily but inefficiently separated by heating to 550-600°C from gangues of comparatively rich sulphidic Sb concentrate. The process is performed in reverberatory furnace under reducing conditions to avoid oxidation of antimony and loss by volatilization, whereas liquid Sb2S3 drips from charge placed in perforated pots or drums. The liquated product, called crude, liquated or needle antimony, is sold for applications requiring antimony sulphide, or – is reduced to metallic state by iron precipitation, or roasted to Sb2O3 followed by reduction in reverberatory furnace. The principal reaction of liquation method is as follow:

$$Sb_2S_3(\text{solid}) \xrightarrow{550-600^\circ C} Sb_2S_3(\text{liquid})$$
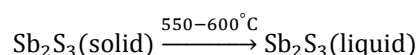
Oxide reduction

Antimony oxide concentrates are reduced to metal with coke or charcoal in reverberatory furnaces at about 1200°C. To minimize volatilization and to dissolve residual sulphides and gangues the alkaline flux is usually used. In spite of this, the loss of Sb from charge by volatilization as Sb2O3 is high (over 15%), so- the effective gas cleaning system should be applied for collection of Sb2O3 dust, that is returned to the charge. The reactions of antimony oxide reduction are as follow:

$$Sb_2O_3 + 3CO \rightarrow 2Sb + 3CO_2$$

$$C + CO_2 \rightleftarrows 2CO$$
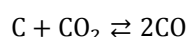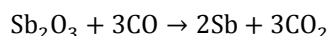
Iron precipitation

This method is intended for rich sulphide concentrates or liquated Sb2S3 (crude antimony), and consists in reduction of molten antimony sulphide by fine iron scrap used in amount slightly exceeding stoichiometric requirement of reaction:

$$Sb_2S_3 + 3Fe \longrightarrow 2Sb + 3FeS$$
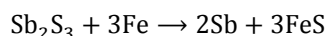
The melted charge is covered with sodium sulphide layer, created by reaction of sodium sulphate with carbon, or the slag is added to create liquid matte with iron sulphide what allows the separation of metallic antimony. As the reduced antimony is contaminated by iron and sulphur - the second fusion with some liquated Sb2S3 and salt is necessary for product purification.

Blast furnace smelting

Medium quality grade of oxide or sulphide or mixed antimony concentrates, and also liquation residues, mattes, rich slags and briquetted fines or dusts are processed in blast furnaces at 1300-1400°C. It is a method of choice

for all fed materials with 25-40% Sb, where the charge mixed with fluxes creates a mixture that prevents losses due to volatilization. The reactions that take place in this method are as follow:

$$2\,Sb_2S_3 + 9\,O_2 \longrightarrow 2\,Sb_2O_3 + 6\,SO_2$$

$$2\,Sb_2O_3 + Sb_2S_3 \longrightarrow 6\,Sb + SO_2$$
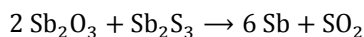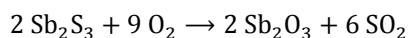
HYDROMETALLURGICAL METHODS

Hydrometallurgical methods are useful for processing all kinds of antimony concentrates. Generally this methods comprise two-stage leaching followed by electrowinning. There are available only two lixiviant systems used for leaching of antimonial charges: alkaline sulphide system and acid chloride system, whereas the former predominates.

The alkaline sulphide system

The leach solution here is a mixture of sodium sulphide or polysulphide and sodium hydroxide. The principal reactions of leaching for sulphidic antimony concentrate are as follow:

$$Na_2S + Sb_2S_3 \longrightarrow 2\,NaSbS_2$$

$$NaSbS_2 + Na_2S \longrightarrow Na_3SbS_3$$

$$4S_{el.} + 6NaOH \longrightarrow 2Na_2S + Na_2S_2O_3 + 3H_2O$$

$$(x-1)S_{el.} + Na_2S \longrightarrow Na_2S_x, (x = 2 \div 5)$$

$$Na_2S_x + (x-1)Na_3SbS_3 \rightarrow (x-1)Na_3SbS_4 + Na_2S$$
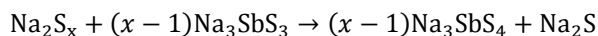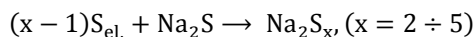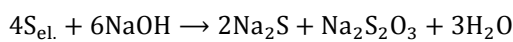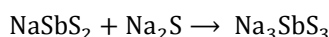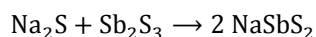
Created sodium thioantimonites (Na$_3$SbS$_3$) and thioantimonates (Na$_3$SbS$_4$) are reduced in electrolytic cells with or without diaphragm according to cathodic reaction:

$$SbS_3^{3-} + 3e^- \rightarrow Sb_{met.} + 3S^{2-}$$
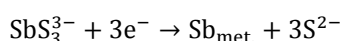
The metallic antimony cathodes after washing could be of substantial purity, over 99.5 wt.%.

The acidic chroride system

The leach solution here comprises hydrochloric acid, often with additions of ferric chloride.

The principal reactions of leaching for sulphidic antimony concentrate are as follow:

$$Sb_2S_3 + 6HCl \rightarrow 2SbCl_3 + 3H_2S$$

$$FeCl_3 + Sb_2S_3 \rightarrow 2SbCl_3 + 6FeCl_2 + 3S_{el.}$$
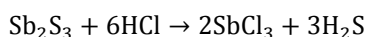
Here ferric chloride is at the same time an oxidizing and chloridizing agent, solubilizing antimony to chloride complex and separating sulfur in elemental form.

The leaching reaction for oxidic antimony concentrate follows the equation:

$$Sb_2O_3 + 6HCl \rightarrow 2SbCl_3 + 3H_2O$$
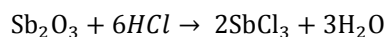
without the need of FeCl₃ presence.

Produced antimony chloride are reduced in electrolytic cells with diaphragms, according to cathodic reaction:

$$Sb^{3+} + 3e^- \rightarrow Sb_{met.}$$
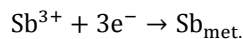
In the case of FeCl₃ presence, it is regenerated according to anodic reactions:

$$Fe^{2+} \rightarrow e^- + Fe^{3+}$$

$$3Cl^- + Fe^{3+} \rightarrow FeCl_3$$
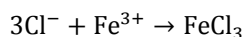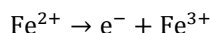
Antimony chloride could be alternatively processed by hydrolysis with precipitation of solid antimony oxychloride, which after ammonia treatment is converted into pure antimony oxide. The mechanism of this treatment is explained by following reactions:

$$SbCl_3 + H_2O \rightarrow SbOCl + 2HCl$$

$$4SbOCl + H_2O \rightarrow Sb_4O_5Cl_2 + 2HCl$$

$$2SbOCl + 2NH_4OH \rightarrow Sb_2O_3 + 2NH_4Cl + H_2O$$

$$Sb_4O_5Cl_2 + 2NH_4OH \rightarrow 2Sb_2O_3 + 2NH_4Cl + H_2O$$
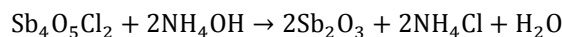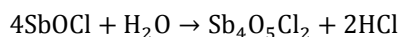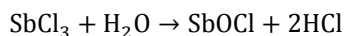
The depicted above hydrometallurgical methods of processing the antimonial concentrates could give directly high grade products ,although they are applied only in limited cases. Alkaline sulphide mode is by far mostly utilized due to its selectivity against antimony and limited corrosivity, compared with acidic chloride mode, which – on the other hand – is being deemed more reliable.
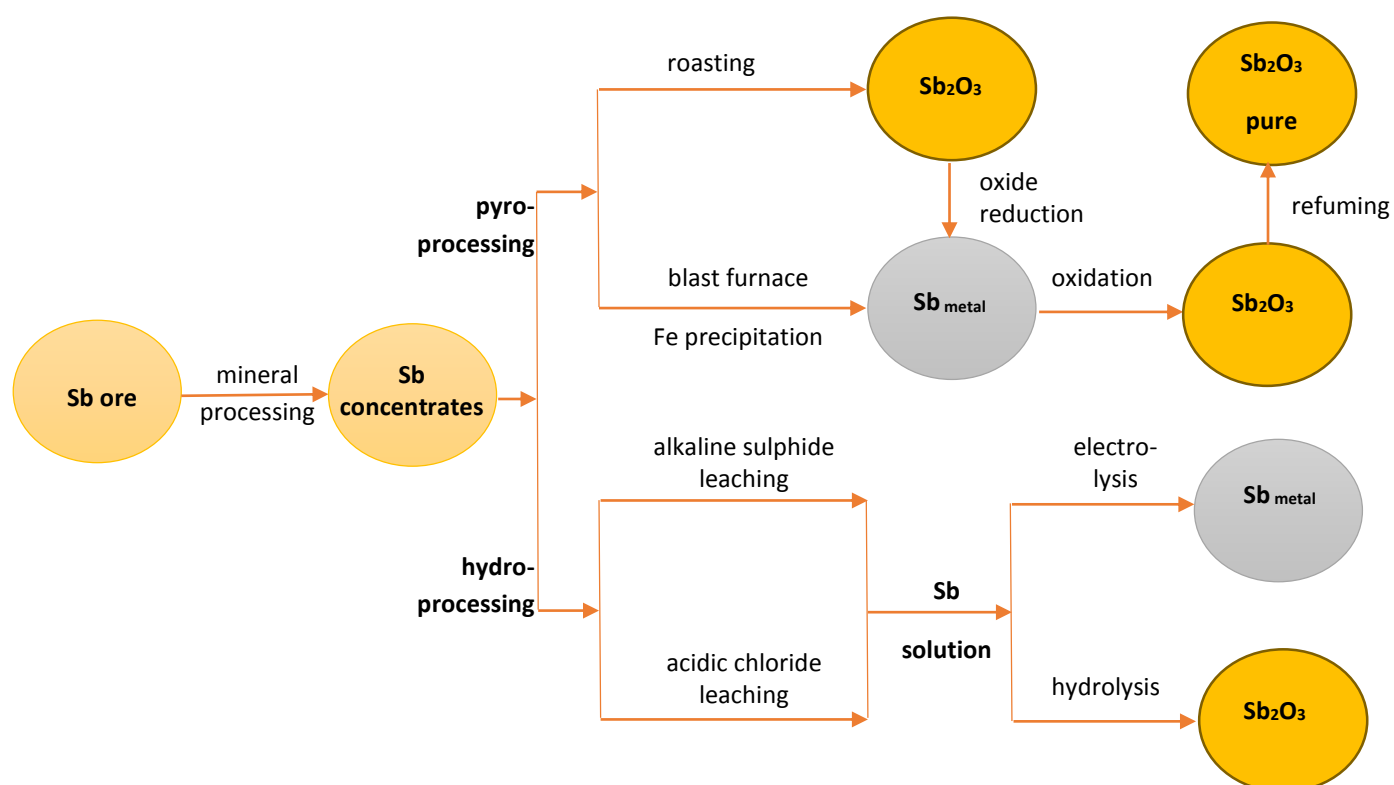
Fig. 1. Simplified diagramme of antimony recovery from primary mineral ores [Dupont, 2016a]

Analysis of typical metallic antimony market products are given in the table below [Anderson 2012].

| wt.% | crude Sb from reductive smelting | crude Sb from precipitation smelting | pure Sb cathodes | pure Sb (Chineese national standards) | | | |
|---|---|---|---|---|---|---|---|
| | | | | I | II | III | IV |
| Sb | 96 – 97 | 80 – 90 | 98 – 98.5 | 99.85 | 99.65 | 99.50 | 99.00 |
| As | 0.2 – 0.3 | 0.2 – 0.3 | 0.02 – 0.1 | <0.05 | <0.10 | <0.15 | <0.25 |
| Pb | 0.1 – 0.25 | 0.1 – 5 | – | – | – | – | – |
| C | 0.001 – 0.01 | 0.03 – 0.2 | 0.004 – 0.005 | – | – | – | – |
| Fe | 0.01 – 0.5 | 3 – 15 | 0.005 – 0.01 | <0.02 | <0.03 | <0.05 | <0.25 |
| Na | 0.02 – 0.1 | 0.02 – 0.1 | 0.1 – 1.0 | – | – | – | – |
| Sn | 0.01 – 0.1 | 0.01 – 0.1 | 0.01 – 0.03 | – | – | – | – |
| S | 0.1 – 1.0 | 0.2 – 0.3 | 0.15 – 0.4 | <0.04 | <0.06 | <0.08 | <0.20 |
| Cu | – | – | – | – | – | – | – |
| sum of impurities | – | – | – | <0.15 | <0.35 | <0.50 | <1.00 |

The typical quality of antimony trioxide usually meets the following specification: $Sb_2O_3$ – min. 99.5 wt.%; As – max. 0.03 wt.%; Pb – max. 0.08 wt.%; Fe – max. 0.01 wt.%; particle size – 0.044 mm – 99.99 wt.%.

Selected manufacturers refine the common antimony grade into high purity antimony (grades 3N; 4,0N ; 4.5N and 5N) in the shape of lump, shot or ingots, used as raw materials for semiconductors, films for optical memory discs or thermo-electron converters, and also produce so called metal C (Cu and Sb metal powder, being a mixture of 50% Sb 99.5 and 50% Cu 99.99, used for electric detonators (e.g. Nihon Seiko Co. Ltd., Japan).

## 2.2.2.2 ANTIMONY RECOVERY FROM BY-PRODUCRS OF PRIMARY COPPER AND ZINC-LEAD CONCENTRATES PROCESSING

Antimony along with lead is present in primary copper and zinc-lead concentrates and in the course of their processing cumulate in crude lead, recovered from by-products (dust, slags, residues, slimes).

Crude lead is directed to pyrometallurgical refinery, where lead impurities are step by step removed into few side byproducts. Some of these lead refining residues and slags contain substantial amounts of antimony associated usually with lead, tin and arsenic. Antimony bearing wastes are further processed by reductive smelting into intermediate PbSnSbAs alloy, which is selectively purified by oxidative drossing of tin and arsenic, into antimonial lead semiproduct. In the end said semiproduct is either diluted with pure lead or enriched with pure antimony, whereby the lead-antimony alloy of a composition meeting the market demand is being manufactured. The simplified flowsheet of antimony recovery from byproducts of primary copper and zinc-lead concentrates processing is presented below.

Recovered in this way antimony in the form of antimonial lead could be applied only to production of grids for lead-acid batteries or munition shots. Further processing is possible but not reasonable from technical and cost effectiveness points of view. Nevertheless, antimony recovered from primary Cu and ZnPb concentrates supplements total Sb supply, and reduces environmental impact of base metals smelting operations.
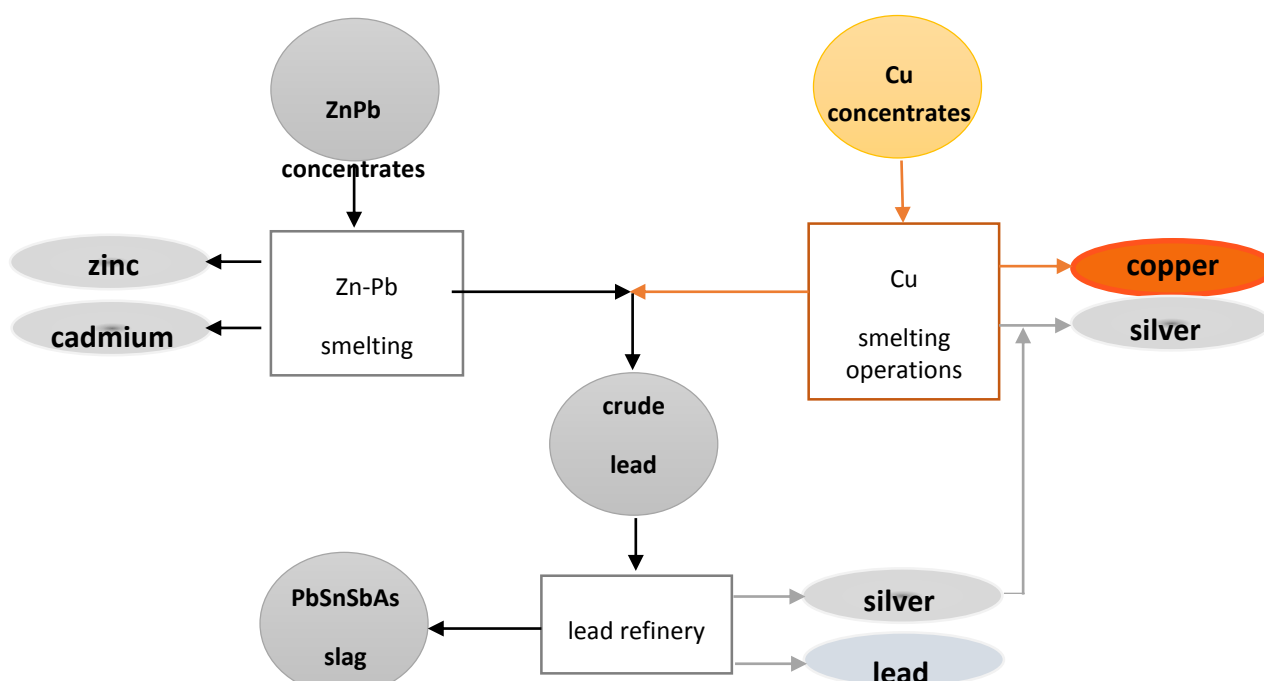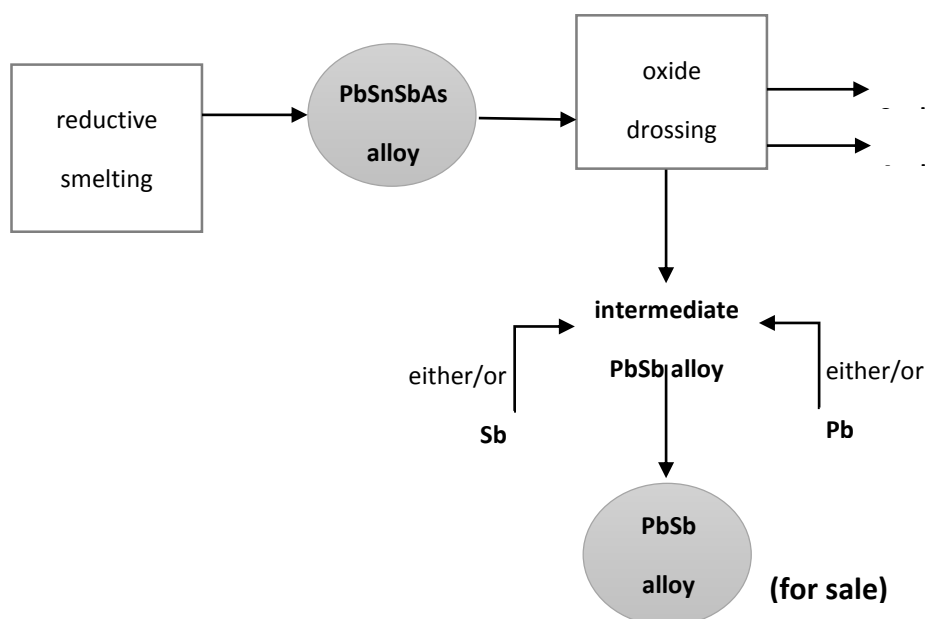
Fig. 2. Antimony recovery from lead byproducts of primary Cu and ZnPb concentrates processing.

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# 3 BARYTE

## 3.1 PRODUCTION LINES OF IDENTIFICATION FROM PRIMARY RESOURCES

### 3.1.1 BARYTE, PRODUCTION AND APPLICATIONS

Baryte or barite ($BaSO_4$) is a naturally occurring barium sulphate mineral ($BaSO_4$). It can sometimes contain strontium, and forms a complete solid solution series to the mineral celestite ($SrSO_4$). Baryte is generally white or colorless depending on the presence of impurities. A commercially important characteristic of barite is its relatively high density of 4.5 g/cm$^3$ (Bonel, K.A, 2005).

World baryte production for 2016 was 7.3 million tonnes. The major barytes producers (in thousand tonnes, data for 2016) are as follows: China (3,100), India (1,300), Morocco (550), United States (430), Turkey (240), Russia (210), Mexico (200), Iran (200), Kazakhstan (190) and Thailand (160) (The Barytes Association, Barytes Statistics).

The main users of barytes in 2016 were (in million tonnes) Middle East (1.74), US (1.60), China (1.50), the European Union and Norway (0.65), Russia and CIS (0.45), South America (0.28), India (0.25), and Africa (0.17) (The Barytes Association, Barytes Statistics).

Baryte is the main industrial source of barium. However, the use of barium metal is minor and baryte is usually used as an industrial mineral (Bonel, K.A, 2005). The main use of baryte (accounting for 88% of 2003 world production) is a weighting agent in oil and gas well drilling fluids or 'mud'.

According to the report of USGS (2009), worldwide 69–77% of baryte is used as a weighting agent for drilling fluids in oil and gas exploration to suppress high formation pressures and prevent blowouts. As a well is drilled, the bit passes through various formations, each with different characteristics. The deeper the hole, the more baryte is needed as a percentage of the total mud mix. An additional benefit of baryte is that it is non-magnetic and thus does not interfere with magnetic measurements taken in the borehole, either during logging-while-drilling or in separate drill hole logging. Baryte used for drilling petroleum wells can be black, blue, brown or gray depending on the ore body. The baryte is finely ground to P97 =75 µm  and -6 µm fraction is less than 30 %wt. The ground baryte also must be dense enough so that its specific gravity is 4.2 or greater, soft enough to not damage the bearings of a tricone drill bit, chemically inert, and containing no more than 250 milligrams per kilogram of soluble alkaline salts.

Baryte's particular qualities of high density, low solubility, high brightness and whiteness, chemical inertness, softness and relative cheapness make it valuable many other applications. Baryte is used in added-value applications which include filler in paint and plastics, sound reduction in engine compartments, coat of automobile finishes for smoothness and corrosion resistance, friction products for automobiles and trucks, radiation-shielding cement, glass ceramics and medical applications (for example, a barium meal before a contrast CAT scan). Baryte is supplied in a variety of forms and the price depends on the amount of processing; filler applications commanding higher prices following intense physical processing by grinding and micronising, and there are further premiums for whiteness and brightness and color (USGS, 2009).   It is also used to produce other barium chemicals, notably barium carbonate which is used for the manufacture of LED glass for television and computer screens (historically in cathode ray tubes); and for dielectrics.

Bonel, K.A, (2005) listed other applications of baryte which include:

as a filler in paint and plastics;

as the main source of barium for the chemical industry;

the production of lithopone, which is a high performance white pigment composed of a mixture of chemically precipitated and calcined zinc sulphide and barium sulphate:

minor uses as an absorber of gamma and X-ray radiation, e.g. special concrete to shield nuclear and X-ray installations; In the construction industry baryte is sometimes added to conctete to increase its density for specialist application; In medicine, it is used to highlight problems within the human body.

in glass manufacture as a flux and to add brilliance and clarity.

## 3.1.2 PRIMARY RESOURCES FOR BARYTE PRODUCTION

World identified resources are estimated at around 740 Mt, of which reserves total 200 Mt (Bonel, K.A, 2005). Baryte deposits are found throughout the world in a variety of geological environments. Three major types of baryte deposits are stratiform, vein and residual. Most baryte is now produced from stratiform deposits (Bonel, K.A, 2005).

Stratiform deposits

The most important stratiform deposits are those formed by the precipitation of baryte at or near the seafloor of sedimentary basins (sedimentary exhalative or 'sedex' deposits). Base metal sulphides (mainly Zn, Pb) are associated.

The largest single deposit is the Mangampet deposit in Andhra Pradesh, India where teo stratiform lenses up to 1.2 km long and 20 m thick contain over 74 Mt of baryte. The most important producer from sedex deposits is China with almost 4 Mt per year. Major deposits occur in Cambrian black shales in the Jiangnan region of south China and the Qinling region in the Yangtze valley. The latter area contains some witherite and barytocalcite $(BaCa(CO3)2)$ deposits associated with the baryte horizons.

Important stratiform baryte deposits occur in the western USA. The largest district is the Nevada baryte belt, which extends over 500 km from north to south and is about 125 km wide containing around 90 Mt of baryte in hundreds of small lenses in siliceous sediments. Important stratiform deposits also occur in late Proterozoic meta-sedimentary rocks near Aberfeldy in Scotland. Other historically important stratiform deposits have been mined from Devonian shales in Germany and in Mesozoic arbonates in a belt from Pakistan through Iran.

Vein and replacements deposits

Small vein-style baryte deposits occur throughout the world, but very few are worked. Large vein-style deposits were mainly worked before the 1980s until large sedex deposits became more important. Vein-style baryte form by precipitation from hot barium-enriched fluids in faults and fractures as a result of fluid mixing or reduced pressure and/or temperature.

## 3.2 PROCESSING TECHNIQUES RECOGNITION AND ANALYSIS

### 3.2.1 MINERAL PROCESSING

Mining methods vary with the type of deposit. Major stratiform depsoits are worked by open pit where this is practicable. The ore is drilled and blasted and then trucked to the mill for pressing. Conventional underground methods are used as appropriated to the shape and attitude of the deposit.

Following initial crushing some baryte is sold as 'direct shipping ore', if it is sufficiently pure. If there are contaminants such as fluorite, quartz, galena or pyrite, gravity separation and flotation are used to separate them after grinding. Then the concentrate is either dried and sold as a powder or processed further for particular applications.

In gravity separation the techniques of washing, desliming, screeninging, jigging and shaking tabling are used. Flotation is used when sulphides (galena, sphalerite, pyrite) and fluorite, calcite associated. Anionic surfactants such as fatty acids, alkyl sulfates, alkyl sulfonates are usually used as the collectors for flotation of baryte from other minerals. Cationic amine collectors are also used. Sodium silicate is used as the modifier.

For which purpose specifications demand a material meeting the drilling "mud" specifications:

1) Fineness: 98% finished product must pass through 200 mesh. (90-95 % will pass through 325 mesh screen.)

2) Specific Gravity: required is 4.3 or better. This product contains 90% or more BaSO4.

3) Viscosity: Maximum viscosity allowed is 60 Centipoise. The usual weight is 16 lbs./gal. on the mud scale.

A flotation Flowsheet is shown in Fig.1 (911metallurgist, https://www.911metallurgist.com/blog/barite-beneficiation-process-plant-flowsheet).

**FLOWSHEET STUDY OF BARITE BENEFICIATION**

Fig.1 A flotation Flowsheet

Barite Ore Crushing Section

The ore is dumped over a 10″ grizzly ahead of the coarse ore bin to control size pieces handled by the crusher. The rugged 36″ x 10′ Apron Ore Feeder, especially designed for the severe service under the feed hopper, has a variable speed drive for controlling the feed to the jaw crusher, thus assuring maximum crushing efficiency. A 2′ wide by 6′ long Shaking Grizzly is operated from the eccentricity of the jaw crusher bumper. The grizzly set at a slope of 15-20° from horizontal saves headroom and with 1.5″ clear openings eliminates the undersize; while oversize material goes to a 15″ x 24″ Jaw Crusher, which reduces the 10″ pieces to approximately 1.5″. A permanent magnet head pulley on the conveyor removes tramp iron present in the ore. A 3′ x6′ Single Deck Vibrating Screen removes the minus fraction from the feed of the 30″ cone-type secondary crusher.

Grinding and Barite Flotation Section

Crude ore is drawn from the fine ore bin by means of a 24" x 14' Adjustable Stroke Belt Ore Feeder and reduced to 100-150 mesh in a 6'x12' Steel Head Ball Mill, charged with 3", 2.5", 2" and 1 diameter balls. The ball mill discharge and spiral screen undersize is classified at approximately 100-150 mesh separation in a 48" x 26'-9" Crossflow Classifier. The classifier sands are returned to the ball mill, while the overflow is pumped by a 3"x3" SRL Rubber Lined Sand Pump to a 12' diameter Hydroclassifier for final separation ahead of flotation. The -200 mesh fraction at approximately 20% solids overflows the Hydroclassifier and flows by gravity to the Super Agitator and Conditioner. The coarse fraction settles, is raked to center discharge cone of hydroclassifier and removed with a 4" Duplex Adjustable Stroke Diaphragm Pump. (The adjustable feature on the classifier acts as a control on the size material overflow.) A restriction plate, in the hydroclassifier tank cone, disperses the added water which tends to eliminate the. "fines" or undersize fraction which might be mechanically trapped in the "coarse" size. The coarse fraction hydroclassifier sands are metered to a 6'x6' Steel Head Ball Mill charged with 1" diameter balls which give more efficient grinding on the fine feed. The ground fraction from the regrind mill is returned to Hydroclassifier with a SRL Sand Pump. This two stage grinding affords added flexibility by controlling grind. Some ores require feed to conditioner to be thickened, which sometimes eliminates troublesome soluble salts and effectively controls the density of the pulp in the conditioner and flotation circuits. Flotation can sometimes be done at 40-50% solids without detriment; yet flotation at higher percent solids produces a more finished product in flotation cells, so this thickener is often included. A 16" Cutter Travel Automatic Sampler, with a wet type cutter between the Hydroclassifier and Conditioner, gives an accurate head sample.

The hydroclassifier overflow, or thickener underflow is conditioned with necessary reagents for flotation. Caustic soda with sodium carbonate are to the conditioner for regulating pH from 8.0 to 10.0. Sodium silicate is sometimes added to liberate slimes; while the collector is usually a refined tall oil acid or similar product. It can be added to conditioner or in stages. An 8-cell No. 21 "Sub-A" Flotation Machine, non-metallic flotation type, equipped with multi-bladed moulded rubber or neoprene impeller and diffuser wearing plates, produces rough flotation concentrates. These rougher concentrates are further upgraded by two stages of cleaning. The flotation tailings are sampled by an Automatic Sampler fitted with a wet type cutter. The tailings are then pumped by means of a SRL Pump to the tailings pond. On the cleaner flotation machine, froth is moved from stage 1 to stage 2 of cleaning via gravity, and the middling rejects from cleaner circuit are returned to the conditioner. A 5" x 5" SRL Sand Pump elevates the final flotation concentrates to the 30' x 10' Spiral Rake Thickener; The thickened product is filtered on a 6' x 6-disc Disc Filter. A 9"x 10' Screw Conveyor feeds the filtered product to the 5' x 50' Countercurrent Dryer with dust collection system. The dried product from the dryers is moved to the Chain Type Bucket Elevator by means of an enclosed screw feeder, and discharged into a dust tight surge bin for a bagging machine; or into a storage bin for loading hopper cars.

## 3.3 REFERENCES

The Barytes Association, Barytes Statistics

USGS, Baryte. 2009 Minerals Yearbook.

Bonel, K.A., 2005. Mineral Profile, Baryte. BGS.

Bonel, K.A., 2005. Mineral Profile, Baryte. BGS.

911metallurgist, https://www.911metallurgist.com/blog/barite-beneficiation-process-plant-flowsheet

# 4   BERYLLIUM

## 4.1   PRODUCTION LINES OF IDENTIFICATION FROM PRIMARY RESOURCES

Beryllium is a chemical element with the symbol Be and atomic number 4. It is a relatively rare element in the universe. It is an alkaline Earth Metal with a density of 1.85g/cm3, with a melting point of 2349 0F (1287 0C) and a boiling point of 4476 0F (2469 0C). It's hardness on the Mohs scale is 5.5.

Pure beryllium is an extremely light, strong and brittle metal and is the second lightest elemental metal after Lithium

### 4.1.1   PRODUCTION FROM PRIMARY SOURCES

Beryllium is primarily produced from two minerals: bertrandite, which contain about 15%wt (Be4Si2O7(OH)2) and beryl, which contains up to 5% wt  (Be3Al2 Si6O18).

Countries with active industrial beryl mining operations are: Brazil, China, Madagascar, Mozambique, Nigeria, Portugal and Rwanda.

Historically, once prominent producers were: Argentina, India and several countries in sub-Sahara Africa countries.

 Other countries produce beryl gemstones: Zambia (which also produced industrial beryl ore).

The United States produced and estimated 90% of the worlds's beryllium in 2015.

The United State, Kazakhstan and China are the only ones known to process beryllium ores and concentrates into beryllium products.

### 4.1.2   PRODUCTION FROM SECONDARY SOURCES

During the production of beryllium, so-called "new" scrap is generated, which usually is returned to the production line and recovered.

"Old" scrap, or end-of-life products containing beryllium are also recycled and beryllium recovered, however only high amounts of materials are reprocessed, such are military aircraft parts or products used in aerospace industry.

There are significant loses due to this fact, and the beryllium contained in smaller components usually dissaperas or is diluted in other waste streams.

### 4.1.3   APPLICATIONS

Due to it's chemical properties, it is a very valued in alloys because of it's high melting point, resistance to creep and shear as well as high tensile strength. Beryllium is six times as strong as steel. It has a similar property as aluminium, forming a protective oxide layer on the surface, thus being resistant to corrosion. Berylium is non-magnetic and non-sparking making it a valuable metal to use in gas and oil applications. It also

have a high thermal conductivity over a large range of temperatures and an excellent heat dissipation properties.

Because of it's low x-ray absorption cross section and high neutron scattering cross section, it's an ideal material for x-ray windows and as a neutron deflector in nuclear applications.

Other applications:

• Consumer electronics and telecommunications;

• Industrial components and commercial aerospace

• Defense and military

• Medical.

Beryllium is highly allergenic, if not handled with care can produce the so-called berylliosis.

## 4.2 REFERENCES

# 5    BISMUTH

## 5.1    PRODUCTION LINES OF IDENTIFICATION FROM PRIMARY RESOURCES

Bismuth is a chemical element with the symbol Bi and atomic number of 83. It is a pentavalent post-transitional metal and one of the pnictogens, very chemically similar to lighter homologues: arsenic and antimony.

### 5.1.1   OCCURRENCE AND PRODUCTION

In earth crust bismuths is twice as aboundant as gold and the most important ores of bismuth are bismuthinite and bismite. Native bismuth is known from Australia, Bolivia and China.

In China and Vietnam, bismuth is a byproduct or coproduct of tungsten and other metal ore processing.

Bismuth is currently recycled to a very low percent, about 5%, from EoL products.

Table 1. Bismuth world mine production and reserves as of USGS 2017 (USG 2017)

| Country | Production – All forms | | Reserves |
|---|---|---|---|
| | 2015 | 2016 | |
| United States | - | - | - |
| Bolivia | 10 | 10 | 10000 |
| Canada | 3 | 3 | 5000 |
| China | 7500 | 7400 | 240000 |
| Mexico | 700 | 700 | 10000 |
| Russia | 40 | 40 | NA |
| Vietnam | 2000 | 2000 | 53000 |
| Other countries | NA | NA | 50000 |
| World Total (rounded) | 10300 | 10200 | 370000 |

### 5.1.2   USES

Bismuth is used in chemicals used in cosmetic industry, industrial laboratory and pharmaceutical applications. Also, it is used in manufacturing of ceramic glazes, crystalware and pearlescent pigments,
Bismuth is considered to be an environmentally friendly substitute for lead in plumbing and many other applications, including fishing weights, hunting ammunition, lubrication greases and soldering alloys.

## 5.2    REFERENCES

(USGS 2017) https://minerals.usgs.gov/minerals/pubs/commodity/bismuth/, (retrieved December 2017)

# 6   BORATES

## 6.1   PRODUCTION LINES OF IDENTIFICATION FROM PRIMARY RESOURCES

Elemental boron is a metalloid which is not found in pure form in nature. Often boron combines with oxygen or other elements to form boric acid or other compounds known as borates. Four borate minerals: colemanite, kernite, tincal and ulexite make up to 90% of the borate minerals used by industry. Boron compounds are bought and sold based on their boric oxide compounds (B2O3).

### 6.1.1   WORLD RESOURCES AND PRODUCTION

The borates deposits are associated with volcanic activity and arid, dry climates, with the largest viable deposits located in the Mojave Desert in the US, the Alpide belt in southern Asia and the Andean belt of South America. The US deposits consists pirmarely of tical, kernite and borates contained in brines and small amounts of ulexite and colemanite. About 70% of all deposits in turkey are colemanite.

Table. X The world production reserved according to USGS (Janury 2017), where the produced amounts in US are withheld (W) due to avoidance in disclosure of the companies proprietary data.

| Country | Production – All forms | | Reserves |
|---------|------|------|----------|
| | 2015 | 2016 | |
| United States | W | W | 40 000 |
| Argentina | 450 | 450 | NA |
| Bolivia | 150 | 150 | NA |
| Chile | 500 | 500 | 35 000 |
| China | 150 | 160 | 32 000 |
| Kazakhstan | 500 | 510 | NA |
| Peru | 240 | 240 | 4000 |
| Russia | 80 | 80 | 40 000 |
| Turkey | 7300 | 7300 | 230 000 |
| World total (rounded) | 9370 | 9400 | 380 000 |

The data from the US production has been withheld, according to USGS, due to the fact that it was desired to avoid disclosure of the proprietary data for the involved companies. It is reported that there are two companies in 2016 which were producing borates in the Southern California (probably Rio Tinto Borax). Also, one of the companies (the leading producer) is mining borate containing ores which are kernite (to produce boric acid), tical (to produce sodium borates) and ulexite (used as primary ingredient in the manufacture of a variety of special glasses and ceramics) by open pit methods (probably the Rio Tinto Borax Mine) and operated associated compound plants. A second company produced borates from brines extracted through solution mining techniques.

The Rio Tinto Borax mine is the largest open-pit mine and the largest borax mine in the world (BOR 2017). According to their public website, the mine is responsible of 30% of the worlds supply of refined borates. Also, they supply nearly 50% demand for the industrial borates serving customers in nearly 100 countries.

### 6.1.2   MAIN USES

Additive in fibreglass for insulation purposes and structural materials, glasses and ceramics, dopant in semiconductors and different chemicals.

One can also characterize the uses as being used as: essentiality (routinely used in agriculture and essential to plants); biostatic (inhibitors of bacterial growth in sufficient quantities); buffering (can balance acidity and alkalinity); glass-forming (borates modify the structure of glass to make it resistant to heat or chemical attack); detergency and cleaning (borates improve the performance of the cleaning products by buffering and conditioning wash water); nuclear shielding (boron is unique among the light elements in its ability to capture neutrons) but also medical applications (boron neutron capture therapy – BNCT); spectroscopic (borates absorb infrared light) – this is a direct application in building products like insulating fiberglass by improving the heat efficiency by preventing the heat loss through infrared transmission; synthesis (used as starting materials in a wide range of advanced materials); cross-linking (borates reacts with suitable alcohols and carbohydrates to link them together) – used in starch adhesives and fluids used for oil recovery; anticorrosion (borates passivate ferrous and other metal surfaces, thus reducing corrosion); fire retarding (borates are used as fire retardants for polymer and cellulosic materials; metallurgical (borates are used to remove oxide impurities from metals). In total, there are over 300 different applications of borates, in different fields.

## 6.2 REFERENCES

(BOR 2017)          https://www.borax.com (retrieved on the 13th of December 2017)

# 7 CHROMIUM

## 7.1 PRODUCTION LINES OF IDENTIFICATION FROM PRIMARY RESOURCES

### 7.1.1 CHROMIUM, PRODUCTION AND APPLICATIONS

Chromium, with symbol Cr and atomic number 24, is a steely-grey, lustrous, hard and brittle metal which takes a high polish, resists tarnishing, and has a high melting point. [21] According to United States Geological Survey in 2012 around 25.6 million tons (the figure is 30.4 million tons in 2016) of chromium from mining chromite ore was produced in the world, dominantly by South Africa, Kazakhstan, Turkey and India, as shown in Figure 1. [1], [2]

| Rank | Country | World Production, By Country (Metric tons, gross weight) |
|---|---|---|
| 1 | South Africa | 11,000,000 |
| 2 | Kazakhstan | 4,000,000 |
| 3 | India | 3,900,000 |
| 4 | Turkey | 2,500,000 |
| 5 | Russian Federation | 660,000 |
| 6 | Oman | 554,800 |
| 7 | Zimbabwe | 550,000 |
| 8 | Brazil | 543,000 |
| 9 | Australia | 452,300 |
| 10 | Finland | 425,217 |
| 11 | Albania | 330,000 |
| 12 | Pakistan | 260,000 |
| 13 | China | 200,000 |
| 14 | Iran, Islamic Republic Of | 100,000 |
| 15 | Madagascar | 67,000 |
| 16 | Viet Nam | 40,000 |
| 17 | Philippines | 23,890 |
| 18 | Sudan | 18,300 |
| 19 | Afghanistan | 6,000 |
| 20 | Greece | 1,600 |



**Chromite ore production by shares**

- South Africa 43%
- Kazakhstan 16%
- India 15%
- Turkey 10%
- Others 16%

Fig. 1 Global mine Cr production by amounts and by shares in different countries in 2012 (in total around 25.6 million tons). [1], [2]

Metal alloys account for 85% of the use of chromium. The remainder is used in the chemical, refractory, and foundry industries. [21]  A article shows that the main field of application of chromium is Ferrochrome with 95.2 %. Other applications have only low-volume uses: foundry 2.4 %, chemicals 1.6 %, refractory 0.8 %. [23]

### 7.1.2 PRIMARY RESOURCES AND CHROMITE

Chromium is the 22nd most abundant element in Earth's crust with an average concentration of 100 ppm. Geographically about 95% of the world's chromium primary resources are located in southern Africa and Kazakhstan. Chromium is mined as chromite ($FeCr_2O4$) ore. About two-fifths of the chromite ores and concentrates in the world are produced in South Africa, while Kazakhstan, India, Russia, and Turkey are also substantial producers. [21]

Chromite is found as orthocumulate lenses of chromitite in peridotite from the Earth's mantle. It also occurs in layered ultramafic intrusive rocks. In addition, it is found in metamorphic rocks such as some serpentinites. Ore deposits of chromite form as early magmatic differentiates. It is commonly associated with olivine, magnetite, serpentine, and corundum. The vast Bushveld igneous complex of South Africa is a large layered mafic to ultramafic igneous body with some layers consisting of 90% chromite making the rare rock type, chromitite. The Stillwater igneous complex in Montana also contains significant chromite. [22]

According to the chemical composition chromite ore is in general classified as different grades, which thereafter leads to different applications. Metallurgical grade chromite ore normally has a Cr/Fe ratio more than 2.0 and contains a minimum of 46-48% of $Cr_2O_3$.[3] This is because the metallurgical grade ore is mainly used for producing ferrochrome, in which the Cr/Fe ratio must be in the order of 3:1. In some cases ferrochrome with around 60% of chromium is also acceptable; therefore chromite ore with lower $Cr_2O_3$ can also be used for metallurgical purpose. At the moment around 96% of chromite ore is used for ferrochrome production, an important intermediate for alloying steels with chromium. According to the carbon content in the ferrochrome ore, the ferrochrome is classified into three grades, i.e., HCFeCr, MCFeCr and LCFeCr (high carbon, medium carbon and low carbon ferrochrome) and the production shares of the three different grades of ferrochrome are 93.7%, 1.3% and 5%, respectively.[4] The end use of the ferrochrome or chromium in the ferrochrome is for steel production (77% used for stainless steel and 19% for alloyed steels).[5] The leading ferrochrome production countries include China, South Africa, Kazakhstan, India and Finland, as shown in Figure 2.
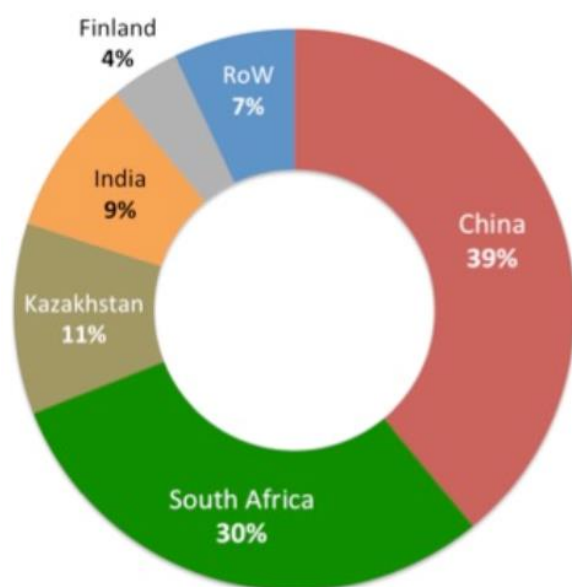


Fig. 2 Global ferrochrome production by shares in different countries.[4]

Besides ferrochrome production a small amount of chromite ore is also used for producing chemicals, foundry sand and refractories. Chemical grade chromite ore usually has high iron content with Cr/Fe ratio being close to 1.0. Refractory grade chromite ore contains relatively large content of $Al_2O_3$ (> 20%) and has ($Al_2O_3$ + $Cr_2O_3$) levels of more than 60%. Foundry grade chromite normally contains more than 44% $Cr_2O_3$, no more than 27% iron and less than 4% $SiO_2$.[3] Due to the improvement in processing technologies one grade of chromite ore can be modified to meet the specification for another grade. Figure 3 shows the usages of chromite ore by products.

In summary, the chromite ore is mainly used to produce HCFeCr, which is substantially used to produce stainless steels.
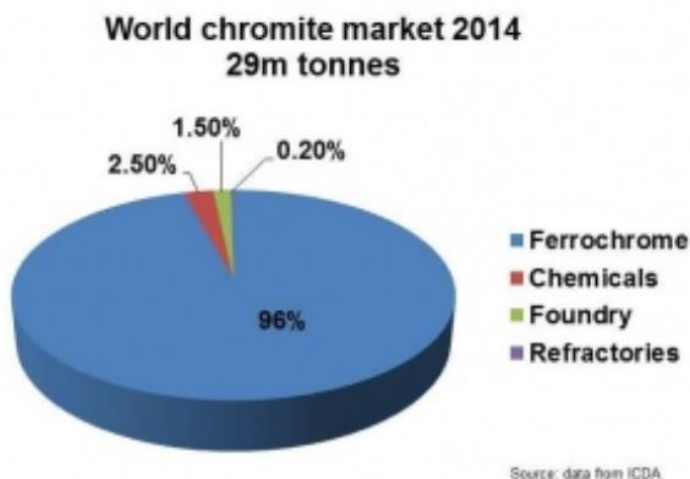


Fig. 3 Usages of chromite ore by products.[5]

## 7.2 PROCESSING TECHNIQUES RECOGNITION AND ANALYSIS

### 7.2.1 MINERAL PROCESSING

To meet the requirement on $Cr_2O_3$ content and sometimes also the Cr/Fe ratio, the raw chromite ore normally needs to be enriched by beneficiation to obtain the chromite ore concentrate. Figure 4 shows a general process flow sheet for chromite ore beneficiation. It is seen that the process include two sections, i.e., comminution and concentration.[6], [7] The comminution step is to grind the chromite ore into reasonable fineness, liberate the gauge materials and thus obtain a material which is suitable for the subsequent unit operations. The concentration step is to obtain the chromite ore concentrate by gravity separator, magnetic separator, etc. In the end chromite ore concentrate is obtained as a marketable product while middling and tailings are reprocessed to recover the valuables or sent to dump.

Due to the shortage of high-grade chromite ore, the use of low-grade chromite ore as well as recovering the values from dumps/tailings is paying more attention to the researchers. At the moment the challenges for processing chromite ore include:[7] (i) reducing the loss of tailing which contains a significant amount of $Cr_2O_3$ (9–20%); (ii) beneficiation of low and sub-grade chromite ore (10–30% $Cr_2O_3$); (iii) recovery of unrecoverable ultrafine chrome particles; (iv) reprocessing of stockpiled tailings containing valuables and (v) producing concentrate with required $Cr_2O_3$ content and Cr/Fe ratio from low grade chromite ore.
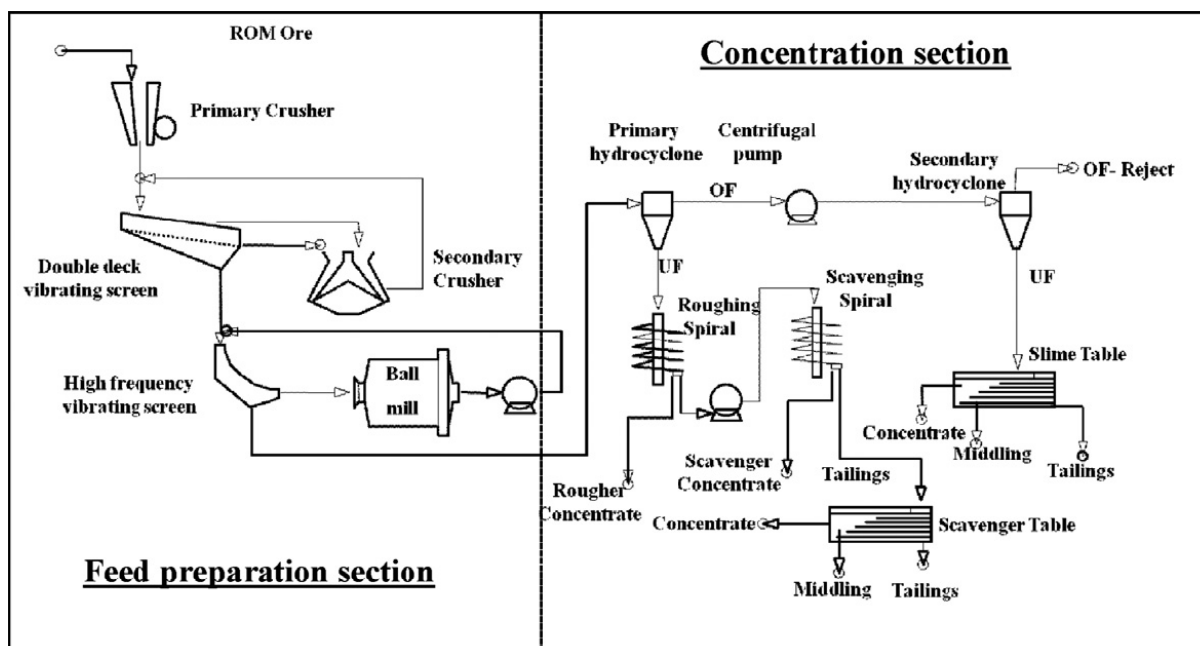
Fig. 4 General process flow sheet for chromite ore beneficiation.[7]

## 7.2.2 METALLURGICAL PROCESSING

### 7.2.2.1 FERROCHROME PRODUCTION

Ferrochrome, especially the HCFeCr, is mainly produced by smelting reduction of chromite ore in the sub-merged arc furnace. The processes developed for ferrochrome production include conventional process, Outokumpu process, DC arc furnace process and Premus process. The input materials include chromite ore (bulk material, pellets or fines), coke/coal, flux materials, etc. The output materials are mainly HCFeCr and slag. The flow of the four processes is shown in Figure 5 and the description of the four processes are shown as follows.[8]–[11]

(a)　　　　Conventional process

In this process chromite ore are cold charged together with coke, coal and quartzite with minimum processing into a submerged AC Electric Arc Furnace. The furnace off-gas (around 1700 oC) is cleaned and vented into the atmosphere. The ferrochrome and slag produced are tapped from the furnace after smelting reduction. The primary advantages of the conventional smelting process are low capital investment and flexibility in terms of raw materials that can be used in the process. However, this process is not energy efficient, as it requires up to 4100 KWh per ton ferrochrome.

(b)　　　　DC arc furnace process

In this process the raw materials can be charged either directly into the DC furnace, or by using a hollow electrode. The primary advantage of this process is that it can utilize any of the available raw materials including 100% chromite fines with minimum or no pre-processing. Further, the process is designed to work

without using coke as a reductant. The significant drawback of the process is the high electric energy consumption (4800 KWh per ton ferrochrome).
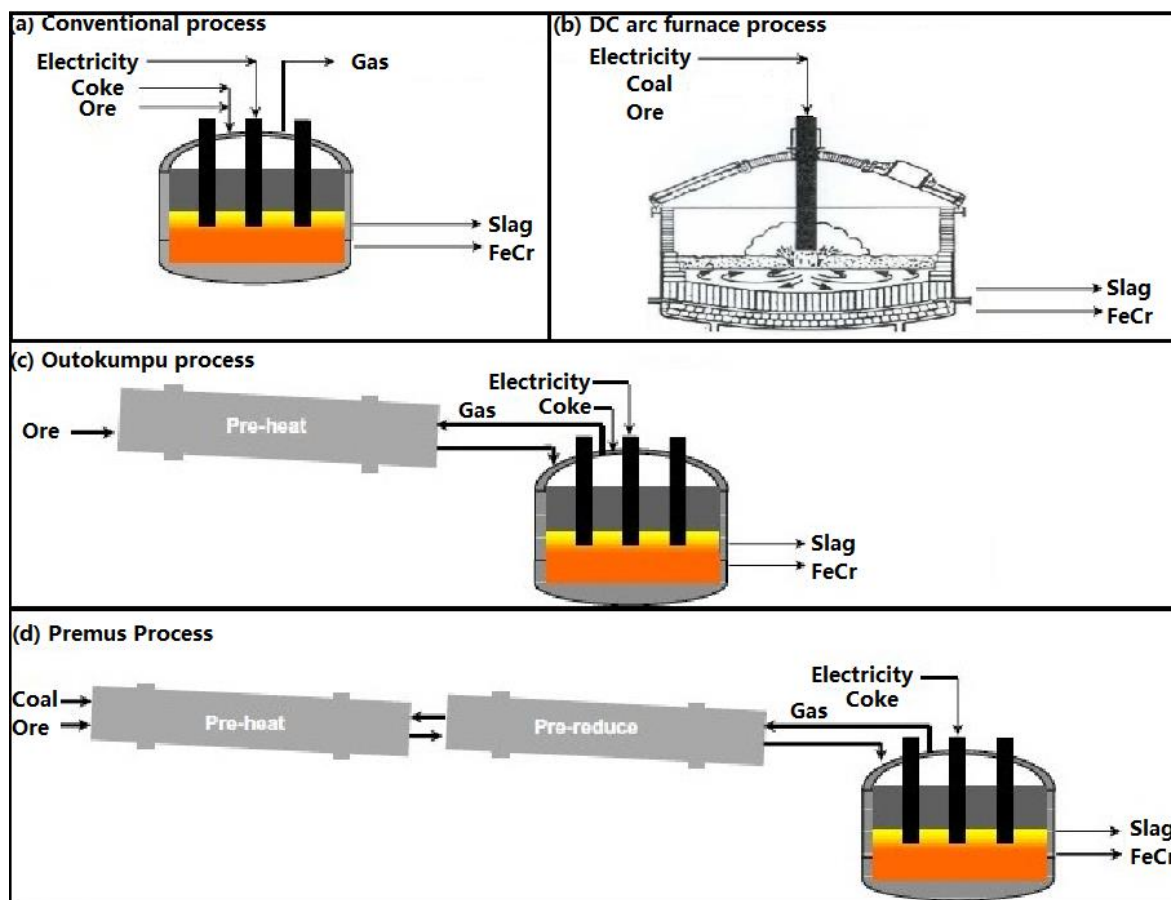


Fig. 5 Ferrochrome production by (a) conventional process, (b) DC arc furnace process, (c) Outokumpu process and (d) Premus process. (Modified from [12], [9])

(c)      Outokumpu process

Outokumpu process involves grinding and pelletizing of ore fines, followed by sintering of green pellets and preheating before smelting. The preheating operation is done mainly in a rotary kiln and the energy required for sintering and preheating the pellets comes from the CO gas generated from the submerged arc furnace. The process provides a means to use the chromite ore fines and the use of hot CO gas for preheating saves the energy required for the smelting reduction. The specific energy consumption for this process is 3500 KWh per ton ferrochrome.

(d)      Premus process

The process involves three stages: sintering, pre-reduction and smelting. The energy required for the prereduciton comes from the furnace hot off-gas and pulverized coal. The pre-reduction process results to the reduction of energy required in the closed submerged arc furnace for final smelting of the ore into ferrochromium. The specific energy consumption for this process is 2400 KWh per ton ferrochrome.

Due to the economic and environmental reasons the Outokumpu process and Premus process will be the dominant processes for HCFeCr production. During smelting reduction of chromite ore 12-16% chromium is lost in the flue dust and slag; further, the high specific energy consumption for the ferrochrome is posing a problem for the ferrochrome-producing countries (e.g. South Africa) where there is a shortage of electricity. Therefore, improving the yield of chromium from the chromite ore as well as developing new technologies using less electricity will be the challenges in the future.

## 7.2.2.2 STAINLESS STEEL PRODUCTION

(a) EAF based stainless steelmaking process[13]

Majority of the stainless is produced in the Electric Arc Furnace (EAF). In this process the ferroalloys (HCFeCr and other alloys), steel scrap, flux materials are charged together into the EAF, where the materials are melted together to produce a crude steel. The produced crude steel could thereafter be refined in the convert. In general, stainless steel making process flow can be classified as duplex or triplex according to the numbers of the used processing units. In duplex process (EAF-AOD process) the crude steel produced from the EAF is refined in the AOD converter, while in triple process (EAF-BOF/AOD-VOD) the crude steel is normally pre-decarburized in a converter (such as BOF converter) and then further decarburized in the VOD converter. The selection of the process routine is dependent on several factors including raw material availability, desired product, downstream processing, existing shop logistics and capital economics. By uring triplex process it is possible to produce high quality stainless steel with low carbon and nitrogen, however, it is at the expense of longer processing time, high refractory cost and higher investment due to the installation of two refining furnaces. The general flow of duplex and triplex process routes for stainless steelmaking is shown in Figure 6.
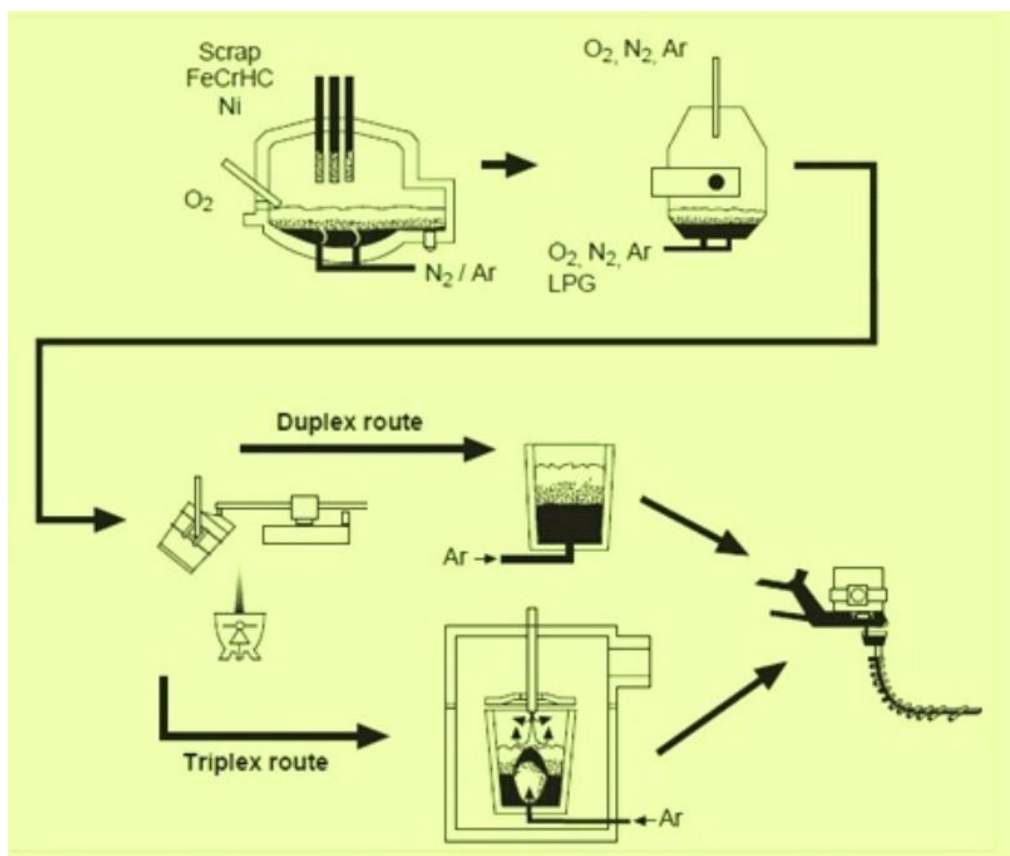
Fig. 6 Comparison of duplex and triplex process routes for stainless steelmaking.[13]

(b) Outokumpu stainless steelmaking process

At Outokumpu (Tornio site) the stainless steels was produced by charging molten ferrochrome produced in-house into the ferrochrome converter and later on mixing molten ferrochrome with melted scrap in the AOD converter.[14], [15] A considerable amount of electric energy is saved due to the integration of the process,[16] since there is no need to cool down, crush and re-melt the ferrochrome. The flow chart of Outokumpu's practice is shown in Figure 7.
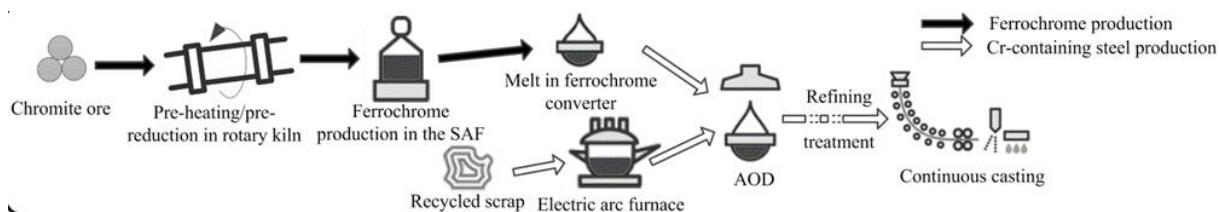


Fig. 7 Integrated stainless steel production process at Outokumpu (Tornio site).

(c) Direct stainless steelmaking process

In Japan some stainless steels were produced by smelting reduction of chromite ore in the converter,[17]–[20] which is also referred to as direct stainless steelmaking process, as the chromite ore is used instead of ferrochrome.  In this process, chromite ore fines or briquettes are injected or charged together with coal/coke

into the high-carbon high-temperature iron melt combined with oxygen blow; instantly the chromite ore can be reduced by the carbon in the high-temperature melt and the reduced chromium would be in situ dissolved in the melt bath, i.e., the steel could be directly alloyed with chromium by the reduced chromite ore. Direct chromium alloying is a highly integrated process, as the ferrochrome production process in the SAF plant and chromium alloying process in a remote steel plant are tailored into one single process.

## 7.3 PRIMARY VALUE CHAIN, IDENTIFICATION OF SECONDARY RESOURCES AND LOSS OF CHROMIUM INTO THE ENVIRONMENT

According to the primary flow of the chromium (chromite ore→ore concentrate→HCFeCr→steels), the primary value chain of the chromium can be drawn, as shown in Figure 8, in which the secondary resources of chromium can be identified and the potential loss of chromium into the environment can be seen as well.

(i)     Low-grade chromite ore and tailing/middling are generated during the mining and mineral processing; some of these materials are reprocessed to recover the valuables while the others are sent to dump due to low economic values.

(ii)     Dust and slag are generated during the smelting reduction of chromite ore in the SAF and EAF-AOD steelmaking process; the chromium in these materials are partially recovered in-house, while the unrecoverable part is either used for other purposes (e.g. construction materials) or sent to dump.

(iii)     Stainless steels are manufactured into various types of products and at the same time some wastes/byproducts (e.g. mill scale) are generated; a part of these materials are recycled while another part is lost in the environment.

(iv)     The stainless steel products in the end of their lives are regarded as EOF products or scrap. A large part of these scrap can be collected to produce new Cr-containing steels while a small part is anyhow lost in the environment due to wear, corrosion, discard, etc.
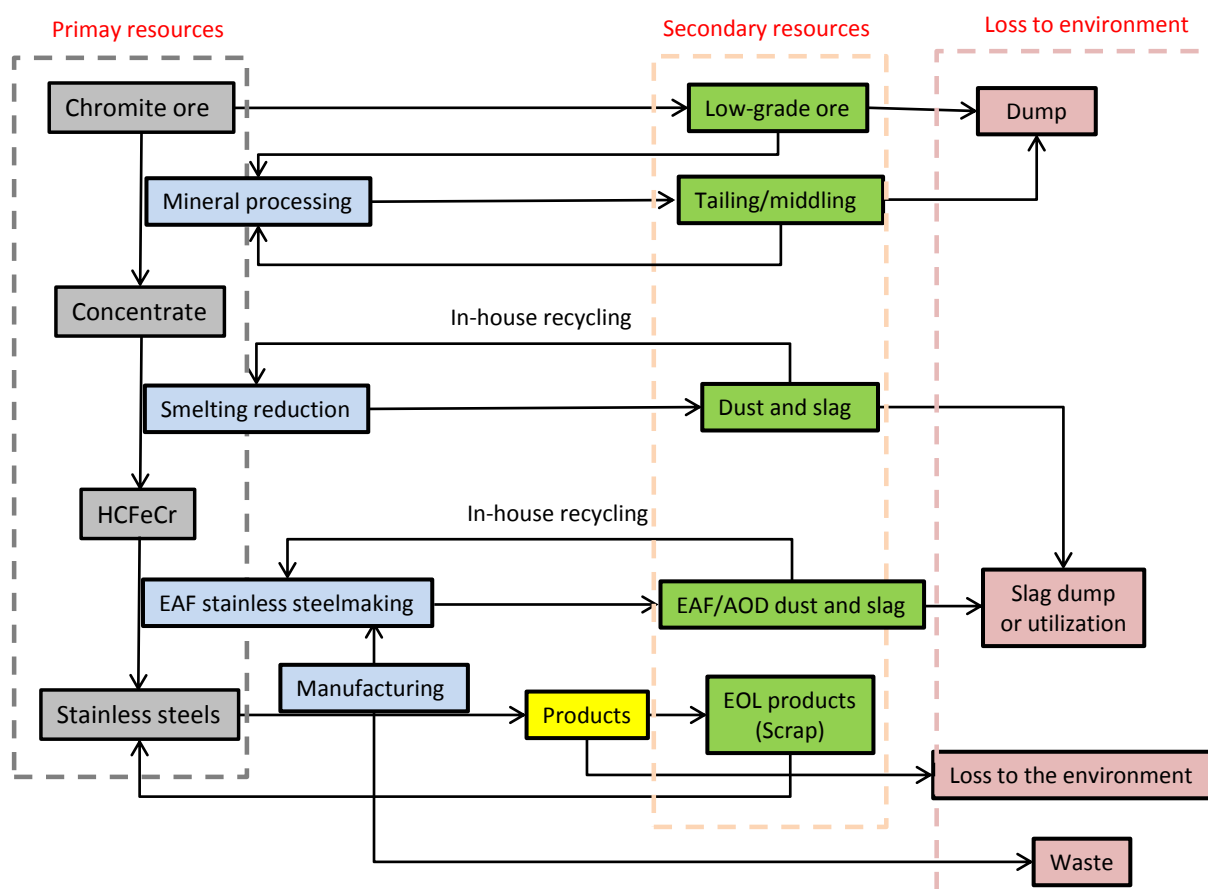
Fig. 8 Primary value chain of chromium.

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## 8    COBALT

### 8.1    PRODUCTION LINES OF IDENTIFICATION FROM PRIMARY RESOURCES

Cobalt is a transition metal belonging to 9 group of elements and iron triad (Fe, Co, Ni). In a free state it is silvery-white metal with blueish shine. It has one stable isotope 59Co. Isotope 60Co (T ½ = 5.27 years) is used as a source of ionising radiation in so called cobalt bombs. Cobalt comprises 0.0025% mass of Earth's crust. It may be often found in nickel ores in the form of arsenic and sulphur compounds. Significant Co concretions may be found also copper ores as well as manganese concretions at the sea and ocean bottoms. Cobalt is mined mainly is Africa. The richest deposits may be found in Central African Copper Belt on the border of Democratic Republic of Kongo (DRC) and Zambia. Main copper and cobalt interests in DRC are dominated by a state-owned mining company Gécamines [1, 2]. China controls the most of the world cobalt production, but it is dependent on deliveries from DRC in 90%. Other countries in which cobalt is mined are i.a. Canada, Brasil, Australia. The global cobalt production from mines decreased to 123.000 tonnes per annum. It is a result of nickel production decline – the most of cobalt production is de facto « waste » from nickel production.The mining structure is almost the same – DRC mined 63.000-66.000 tonnes per annum, while Austalia 5.000-6.000, Canada 7.000, Cuba 4.200, Magadascar 3.300 tonnes, Russia 6.200 tonnes, Zambia 4.600, China ca. 7.000 tonnes. The prodcutionin other countries is significantly lower. Figure 1 shows the market share of global corporations in cobalt production.
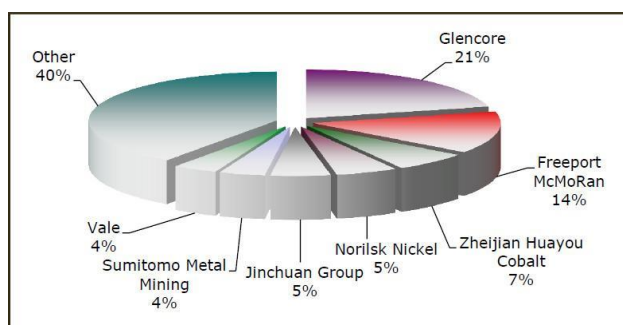


Fig. 1 Market share in global cobalt production **[4]**

Cobalt application fields may by divided into two broad gropus : chemical and metallurgical (Fig. 2). Chemical applications covers batteries, mainly lithium-ion batteries for electric vehicles (EV) as well as laptops, personal computers, smartphones etc. The main metallurgical applications are high-temperature alloys. Cobalt may be also found in superalloys (rotating parts in aviation, defence, energy generation, thermal sprayers, prosthetics etc.), high speed steel, carbide and diamond tools and magnets.

# Cobalt Applications & Growth

## 2016 Cobalt Demand & Mid-term Growth Forecast

**6.0% CAGR All Refined Cobalt**

**7.1% CAGR Cobalt Chemical Applications**

- Superalloys — 15%
- Metallurgical Applications- Other — 22%
- Batteries — 46%
- Chemical Applications- Other — 18%
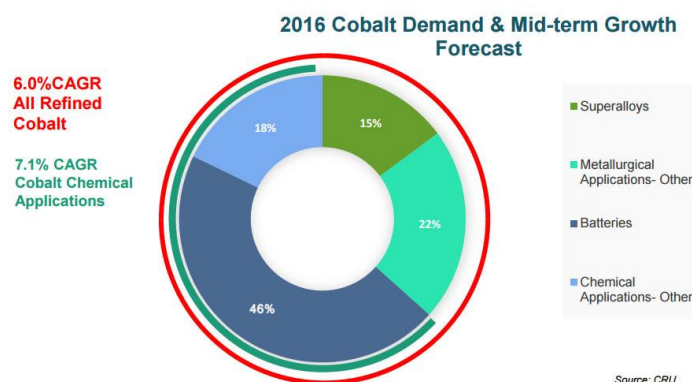
Source: CRU

Fig 2. Cobalt applications and growth in 2026 [source: CRU].

In recent years cobalt demand is growing mainly due to chemical (batteries) sector. Cobalt production increase, price changes and forecast to 2021 are shown in Fig. 3.

# Cobalt Supply, Demand & Price

## SUPPLY/DEMAND BALANCE & PRICE FORECAST

$23.50

- 20.5% Co Sulfate
- 99.3% Co
- SD Balance (non-metallurgical)
- SD Balance (metallurgical)
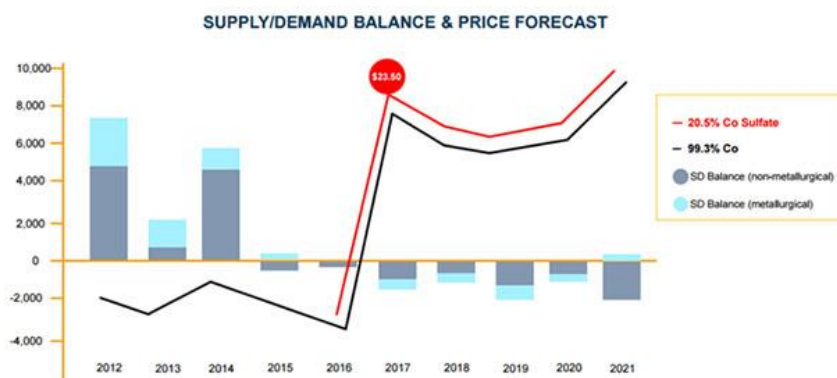
Fig. 3. Cobalt supply, demand and price. Current situation and forecasts until 2021 [source: CRU]

## 8.2 PROCESSING TECHNIQUES RECOGNITION AND ANALYSIS

Cobalt production involves such processes as extraction, flotation, leaching, electolysis. The final product of processes may be either pure metal or crude contaminated cobalt product for further refinning or for sale.Depending on market demand products of wide range specific phisical and chemical properties may be manufactured. In order to assure specific properties (e.g. desired grain size or purity) carboxylate pyrolysis, high-temperature oxide reduction, precipitation and crystallisation techniques are applied. These processes are often patented, confidential and very specific to production site **[5].**

### 8.2.1 MINERAL PROCESSING

## 8.2.1.1 CENTRAL AFRICAN COPPER BELT ORES

Main cobalt minerals which may be found in Earth's crust are smaltite $CoAs_2$ (5-16% Co) and cobaltite CoAsS (35.53% Co). The highest cobalt content has linnaeite $Co_3S_4$ (57.96% Co), erythrite $Co_3[AsO_4]_2 \cdot 8H_2O$ (37.54% Co) and cobaltite. However, the most important are sulphide sources (Zn-Cu-(Pb)) and copper-cobalt ores of Central African Copper Belt on DRC and Zambia border. Its location is shown in Fig. 4.
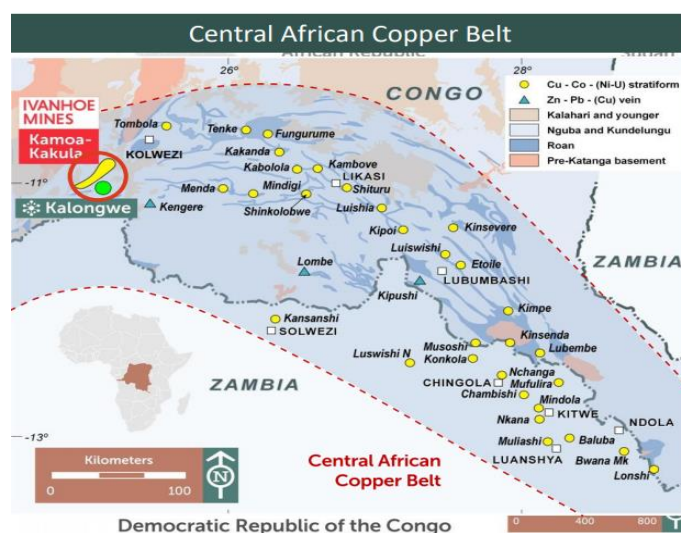


Fig. 4. Location of main deposits in Copper Belt [6]

These ores are processed in a conventional way to produce copper-cobalt concentrate. Then, it is floated to separate cobalt enriched concentrate.  Copper Belt ores are mainly sulphides and oxides. Formerly, most of cobalt was obtained by flotation in Roast-Leach-Electrowin process (RLE). It was composed of sintering (sulphides), atmospheric leaching using sulphuric acid and direct copper electrowinning. In recent years (except of few old plants), in order to adjust products to London LME Grade "A" requirements, electrowinning process was substituted by solvent extraction-electrowinning (SX-EW). Nickel sulphide deposits were in the past processed by flotation followed by smelting. Then, hydrometallurgical processes were used for nickel, copper and cobalt recovery. There are many refining processes of this kind including: ammonia washing, eg. Sherritt-Gordon process in which LME grade nickel briquettes and cobalt are obtained by hydrogen reduction; "modified" Sherritt-Gordon process (washing under pressure oxidation conditions), e.g. Impala BMR, South Africa; oxidative sulphate leaching, e.g. Outokumpu; chlorine leaching according to Xstrata Nikkelwerk (e.g. Falconbridge/Kristiansands), where cobalt is recovered by electrolytic chlorination. Other methods are electrorefining of matt nicklel anodes (Jinchuan and Inco, Thompson), or electrofiltration of contaminated metal (Russia).

## 8.2.1.2 LATERITE

Since 2012 nickel laterite importance has increased. Sulphide supply is gradually decreasing and laterite processing is continuously improved. Formerly, laterites were processed only in pyrometallurgical processes. Hydrometallurgical operations were first used in Nicaro plant (Cuba) within Caron process. Then, in 1959 in Moa Bay (Cuba) high pressure acid leaching was used (HPAL). The main advantage of these hydrometallurgical processes is the possibility of cobalt recovery, which was not possible with sole application of pyrometallurgical

methods. Since 1974 growing trend in hydrometallurgy application for higher grade laterites (mainly cobalt-containing limonites) is observed [5]. Currently, HPAL together with variety of nickel and cobalt production processes is preferred. The examples are Bulong, Cawse and Murrin Murrin (beginning 1999), Coral Bay (2005), Ravensthorpe (2007), Goro (2010), Ambatovy (Madagascar, 2011). In 20th century in cobalt processing processes arsenic ores were used. Roasting and pressure leaching were applied. Due to health and environmental concerns almost all these plants were closed. Only Moroccan facility (CTT) is still open. Reopening in Canada and USA was also planned.

## 8.2.2 METALLURGICAL EXTRACTION

The overall scheme of possible cobalt production stages is shown on Figure 5.
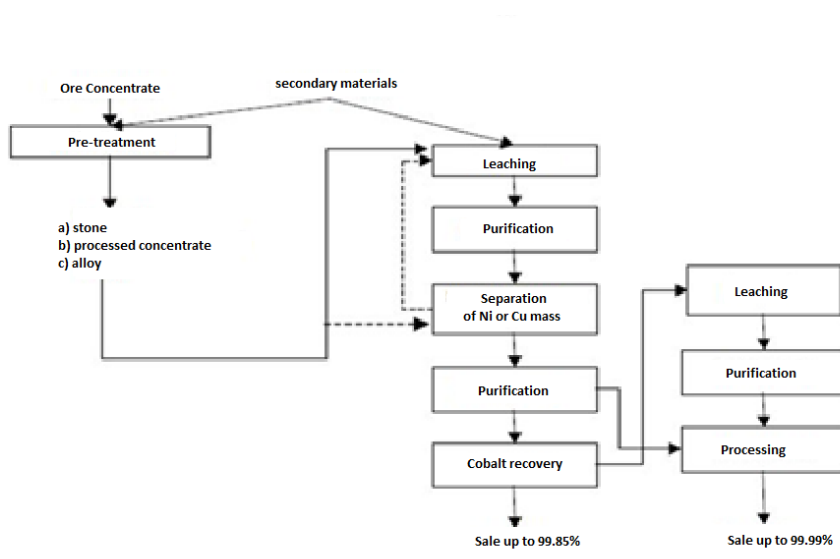


Fig 5. Overall technological scheme of possible cobalt production stages

The classical way to obtain cobalt is the process of slurry smelting. In Europe only one furnace is applied to such process, in Outokumpu. There are also five more institutions that utilize this operation in the rest of the world. Two of them use suspension roasters designed by Western Mining Corporation, where furnaces to smelt and purify dross were built together, forming one, bigger unit. Cobalt mattes obtained in smelting processes need to be processed further in order to recover and purify the metal present in mattes. The example of such process is DON (Direct Outokumpu Nickel) process, applied in Outokumpu (Figure 6).
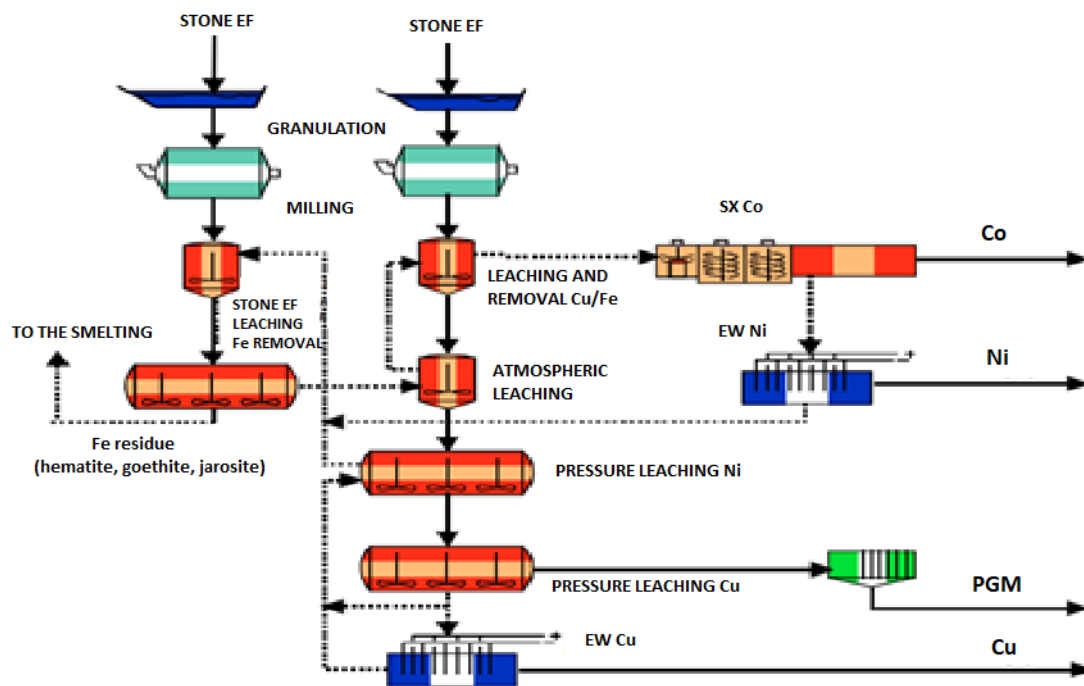
EF - electric furnace, FSF - suspension smelting furnace, EW - electrowinning

Fig. 6. *Technological scheme of DON process.* Method 1

## 8.2.2.1 SCHERRITT PROCESS

Sherritt process is a hydrometallurgical process called Sherritt Gordon Mines Ltd. (currently Sherritt International), applied in Sherridon and Lynn Lake Manitoba Canada, which is based on superior Forward process, elaborated by dr Frank Forward, which goal is copper and nickel recovery from the same mines. Nickel sulfide concentrates could be processed in various manner: roasting; smelting, in order to produce mattes, which are further processed to obtain nickel and cobalt; or pressure leaching with ammonia solution. The residue is discarded. The concentrate contains about 0.4% of cobalt and 30% of sulfur, and is leached under pressure in higher temperature, with ammonia solution. Copper precipitates in a form of copper sulfide. Nickel powder (>99%) is then reduced with hydrogen under pressure and higher temperature. From remaining solution, which contains approximately equal ratio of nickel and cobalt sulfides, the mixed sulfides are precipitated, and the liquid condenses and crystallizes to ammonium sulfate. Obtained mixed sulfides are further processed by pressure leaching. Then ammonia is added to remove potassium and iron in a form of jarosite ($KFe^{3+}_3(OH)_6(SO_4)_2$). Nickel is removed in a form of hydrated nickel-ammonium sulfate ($(NiSO_4)\cdot((NH_4)_2SO_4)\cdot6H_2O$, from which metallic nickel is obtained. Cobalt powder of about 99.6% purity is precipitated from the residue (Figure 7).
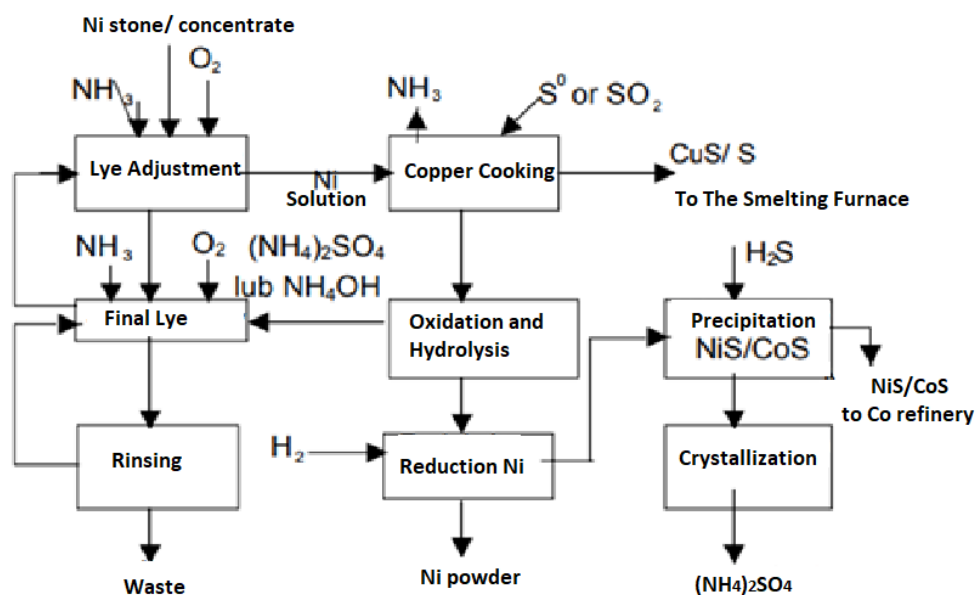
Fig. 7. Scheme of Scherritt leaching process with ammonia.

## 8.2.2.2 SOLVENT EXTRACTION

Cobalt is produced during nickel recovery after the separation with solvent extraction (SX) technique. For cobalt extraction present in ores from Katanga region in Democratic Rebublic of Congo, D2EHPA extractant is used. Previously implemented LIX 984 was effective on Cu extraction, however it was non-selective in Zn and Co extraction. D2EHPA application allowed to achieve the cobalt recovery of over 90% (Figure 8).
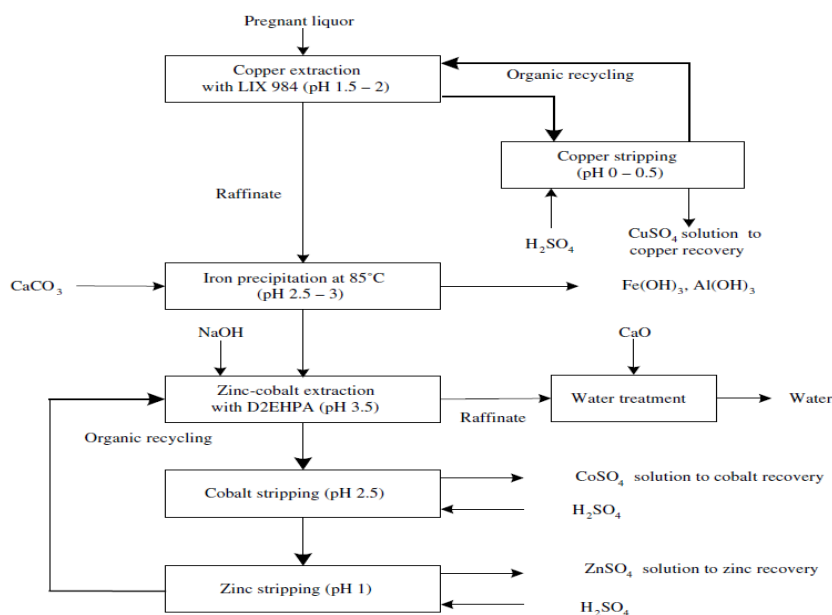


Rys. 8. *Scheme of Cu, Zn and Co processing using solvent extraction in mixing sedimentation tank.* [7].

## 8.2.2.3 OLDSHUE-RUSHOT

Recently there was proposed a method of cobalt sulfate solution extraction with D2EHPA/TBP mixture, in extraction column, applied in a pilot plant in Oldshue-Rushton, after the previous ore leaching with sulfuric acid (Figure 9). The results showed that the extractant mixture of D2EHPA/TBP allows to obtain the extraction performance of 93%, and stripping efficiency of 91.5% with rotor speed of 220 rpm [8].
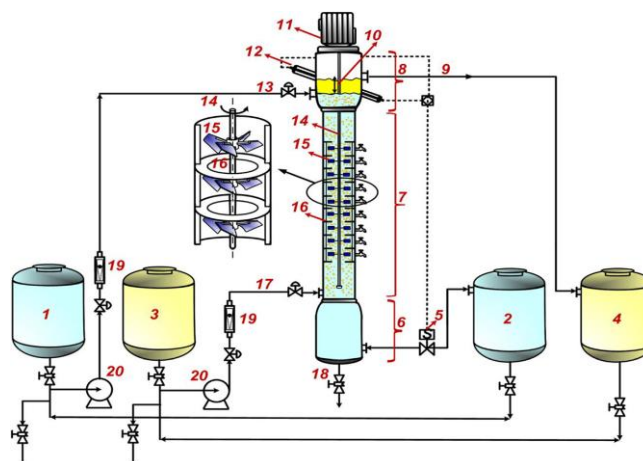


Fig. 9. Oldshue–Rushton schematic illustration: (1) & (2) aqueous phase reservoirs; (3) & (4) organic phase reservoirs; (5)solenoid valve; (6) bottom separation region; (7) extraction region; (8) top separation region; (9) extract stream output; (10)extract and raffinate streams interface height; (11) electric motor; (12) optical sensor; (13) continuous phase input; (14) rotorshaft; (15) 6-blade impellers; (16) stator; (17) organic phase input; (18) raffinate stream output; (19) flow meter; (20) pump.

## 8.3 MINE TAILINGS AND RESIDUES PROCESSING AND POTENTIAL UTILIZATIONS

### 8.3.1 PROCESSING

 The increasing cost of mineral resources acquisition in global mining sector results in increasingly more complex utilization of resources, especially various mineral wastes. For such purposes, appropriate technical apparatus is implemented, such as gravity concentrators, whose task is to recover precious trace constituents from post-flotation wastes, especially of non-ferrous metals ores. The crucial factor of profitability of such undertaking is that if the constituents in such waste are in released state, which allows to exclude the high-cost milling pretreatment process. This technology is implemented in e.g. Palabora Mining in the Republic of South Africa, or Climax and Timmins in Canada. Palabora Mines owns the largest installation of such type, where minerals of uranium, zirconium and residual copper are recovered from post-flotation wastes of copper ores, using gravitational methods (Reichert cones). This technology is found to be highly profitable. Copper flotation step is generally non-efficient for cobalt production (up to 40% fo oxides and up to 80% for sulfides). Considerable amount of cobalt is present in mining wastes, which can be recovered. Kolwezi Tailing Project could be an example, where cobalt is recovered while environment and social circumstances are being improved. Before starting this project, 100 years of mining history were taken into consideration, including: extensive pits, rock waste and mining deposit waste landfills, a city of 200 000 population nearby, some villages in concessive area, natural resources acquisition necessity, changes of cultivation due to polluted main river valley, extreme air

pollution [**9**]. Large amount of post-flotation wastes of copper and cobalt ores are stored in Katanga region in Democratic Republic of Congo (DRC). In some cases wastes containing copper and cobalt in remunerative to restore concentrations. Kambove Koncentrator (DRC) implement copper and cobalt recovery through reprocessing of post-flotation wastes of copper and cobalt ores [**10**]. The cobalt content in wastes from ore processing is different. For example, Kolwezi Tailings Project refer to 112,8 Mt of wastes containing 1.49% of copper and 0.32% of cobalt, while wastes in Kambove Koncentrator (DRC) contain approximately 1.69% of copper and 0.61% of cobalt.

## 8.3.2  POTENTIAL UTILIZATIONS

Cobalt recovery from mine waste dump is carried out with water extraction under high pressure, acid leaching, solvent extraction and electrowinning. Currently applied, and constantly improved installations allow to restore up to 76% Co and 93% Cu (in Kambove Koncentrator the recovery was even 99.7% Cu and 87% Co). The main disadvantage of this process is that it requires large amounts of reagents. It was found that reprocessing of wastes in Kambove Koncentrator (DRC) is profitable, because it reduces the negative impact of processing industry on environment. It could also contribute to protect the natural resources through recovery of metals from wastes produced in metallurgical processes.

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# 9   COKING COAL

## 9.1   PRODUCTION LINES OF IDENTIFICATION FROM PRIMARY RESOURCES

### 9.1.1   COKING COAL, PRODUCTION AND RESERVES

Coking coal is a special group of coals belonging to hard coals that are of bituminous type. The property that really sets coking coals apart from other coals is caking ability, which is the specific property required in order to make coke suitable for making steel. When heating a coking coal without presence of air the coal becomes plastic and swells at about 350-500°C and solidifies and shrinks when further heated to 500-1000°C. As can be seen from Figure 1 the production of hard coals in Europe is mainly in Poland and Ukraine but there is some minor production also in UK, Germany, Czech Republic, Spain and Turkey.



Figure 1 Production of hard coal in Europe[1]

As can be seen from **Error! Reference source not found.**, regions with largest hard coal reserves are North America, Russia, China, India and Australia. Looking closer into the qualities it can be seen that the quality of coals from China and India are of lower. Reserves of coal and lignite are abundant and total resources are estimated to be 17 449 billion tonnes of coal equivalent (Gtce) of which only 1.2% have been extracted so far. In Europe the hard coal reserves are estimated to be approximately 17.6 Gtce.

Figure 2 Global hard coal and lignin reserves

The production of hard coal in Europe has decreased 23% from 1990 to 2016, in 2016 approximately 36 % of the hard coal was produced in Europe and 74% imported. The total use of hard coal has been quite unchanged and in the range of 360-380 Mt, the origin of the imported part 230-245 Mt is shown in Figure 3.

The main part of the coking coal is imported to Europe from North America and Australia and the selection of coal types depends both on the desired coke quality and the final metal product quality as some component in ash may dissolve in the metal, e.g. phosphorus. As can be seen from Table 1 both Australia and US has a net production while EU-28 and steel producing countries like Japan and North Korea without own coking coal sources have a large consumption. In fact, although the amount of coking coals produced are high in China there is a significant import of high quality coking coals. Also India has coking coal but this has in some cases undesired quality for use in ironmaking.
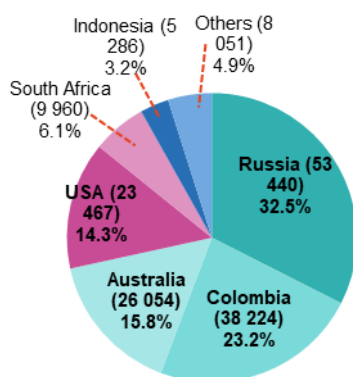


Figure 3 Origin of hard coal imported to Europe[1]
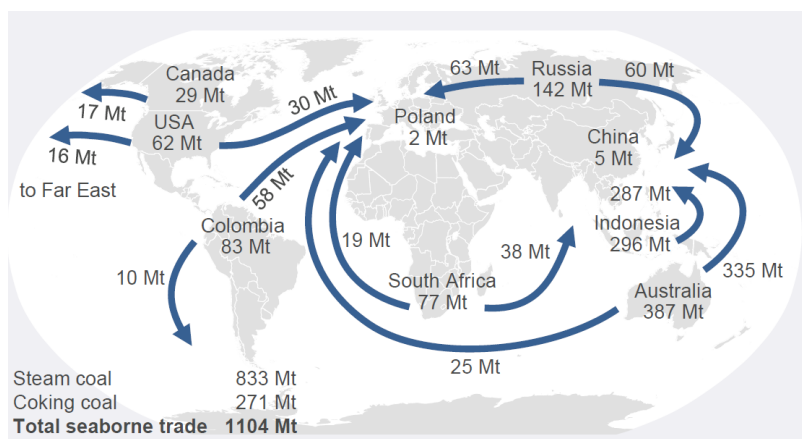
Figure 4 Global trading of steam coal and coking coal[3]

The need for coking coal follows the economic situation for steel making and when to steel production rises the coking coal cost is also increased. Specific circumstances as e.g. rain and flooding I Australia recently caused difficulties to purchase some specific coking coals and it also had effect on the availability of coking coal.

Table 1 Largest global coal producers and consumers with the amount and ratio of coking coal indicated, data collected from EURACOAL[3]

| Largest coal producers | | | | Largest coal consumers | | | |
|---|---|---|---|---|---|---|---|
| | Coking coal, Mt | Tot. coal prod Mt | Ratio of coking coal | | Coking coal, Mt | Tot. coal prod Mt | Ratio of coking coal |
| China | 611.1 | 3527.2 | 17.3% | China | 658.1 | 3752.5 | 17.5% |
| **United States** | **57.4** | 812.8 | 7.1% | India | 105.6 | 912.3 | 11.6% |
| India | 54.5 | 691.3 | 7.9% | United States | 17.6 | 713.3 | 2.5% |
| **Australia** | **191.1** | 508.7 | 37.6% | **EU-28** | **59.9** | 686.9 | 8.7% |
| **EU-28** | **20.9** | 498.9 | 4.2% | Russia | 59.7 | 218.9 | 27.3% |
| Indonesia | 2.7 | 469.3 | 0.6% | Japan | 50.3 | 191.5 | 26.3% |
| Russia | 78.0 | 349.3 | 22.3% | South Africa | 4.0 | 176.0 | 2.3% |
| South Africa | 3.2 | 252.1 | 1.3% | South Korea | 38.9 | 139.3 | 27.9% |
| Kazakhstan | 16 | 107.2 | 14.9% | Australia | 3.9 | 122.2 | 3.2% |
| Colombia | 4.7 | 90.3 | 5.2% | Turkey | 6.2 | 87.3 | 7.1% |
| Others | 50.3 | 401.6 | 12.5% | Others | 67.3 | 705.7 | 9.5% |
| World | 1089.9 | 7708.7 | 14.1% | World | 1071.5 | 7705.9 | 13.9% |

## 9.1.2 APPLICATIONS

Coking coal is mainly used for production of metallurgical coke, the production of coke in Europe was 29384 kt in 2016, see Figure 5. The amount of coking coal needed for the production of coke varies dependent on the volatile content but approximately 1250-1400 kg coking coal is needed for the production on 1 t of coke. The amount of coking coal corresponding to the coke production in 2016 is following 36 730 - 41 138 kt of coking coal.
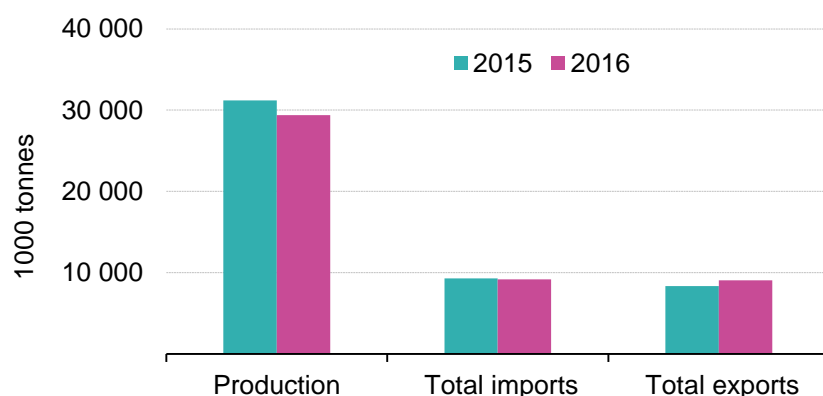
Figure 5 Production, import and export of coke in EU-28 2015 and 2016[1]

A distinction is made between medium rank coking coals (vitrinite reflectance 1.0% up to about 1.8%) and lower rank coking coals (vitrinite reflectance about 0.7% to 1.0%), classified as hard and soft coking coals (HCC and SCC), respectively, as based on the type of coke produced from them. In general a blend between HCC, medium coking coals (MCC) and SCC as to achieve high quality coke but at the same time keep the raw material cost at reasonable levels. As the volatile matter decreases with increasing coal rank the coke yield will increase when shifting to high rank coals. Moreover, as reaction of C in coke with $CO_2$ in the in-furnace atmosphere will lower the strength. Coke with low reactivity is desired. This is as well linked to the coal rank and its reflectance but also to the ash composition. It is desirable with acid ash, with high comparably high contents of $SiO_2$ and $Al_2O_3$, and low contents of iron oxide, CaO and alkalis that are known to catalyze the gasification reaction.

High quality metallurgical coke is mainly used in blast furnace iron making but also in other metallurgical processes as e.g. ferroalloy production while foundry coke can be used in low shaft furnaces and cupolas producing metals but in some cases also fibers for insulation.

Table 1 International classification of seam coals[5]

| LOW-RANK COAL | | | MEDIUM-RANK COAL | | | | HIGH-RANK COAL | | |
|---|---|---|---|---|---|---|---|---|---|
| C | B | A | D | C | B | A | C | B | A |
| LIGNITE | | SUB- | BITUMINOUS | | | | ANTHRACITE | | |
| ORTHO | META | BIT | PARA | ORTHO | META | PER | PARA | ORTHO | META |
| | 0.5 | | 1.0 | | 2.0 | | 4.0 | | |
| | 0.4 | | 0.6 | | 1.4 | | 3.0 | | 5.5 |

- - - - Mean random vitrinite reflectance - - - - - - - - - - - - - - - - - ->

## 9.2 PROCESSING TECHNIQUES RECOGNITION AND ANALYSIS

### 9.2.1 MINERAL PROCESSING

Coal mining may be either through surface or underground mining, for underground mining via long wall or room-and-pillar mining. Coal mined is often inconsistent in size and contains impurities such as ash and needs

to be processed to a more consistent quality. An example of a coal beneficiation or coal washing preparation plant is shown in Figure 1.[2]

In general, crushing reduces the overall top size of the coal so that it can be more easily handled and processed and the crushed material is classified using screen, cyclone etc. The coal is washed and often some flotation method is used, after the separation step for heavy gangue and light coal the material is dewatered. Washing water is collected and reused. Wash coal for delivery to customer is prepared by mixing courser and finer fractions.[4]
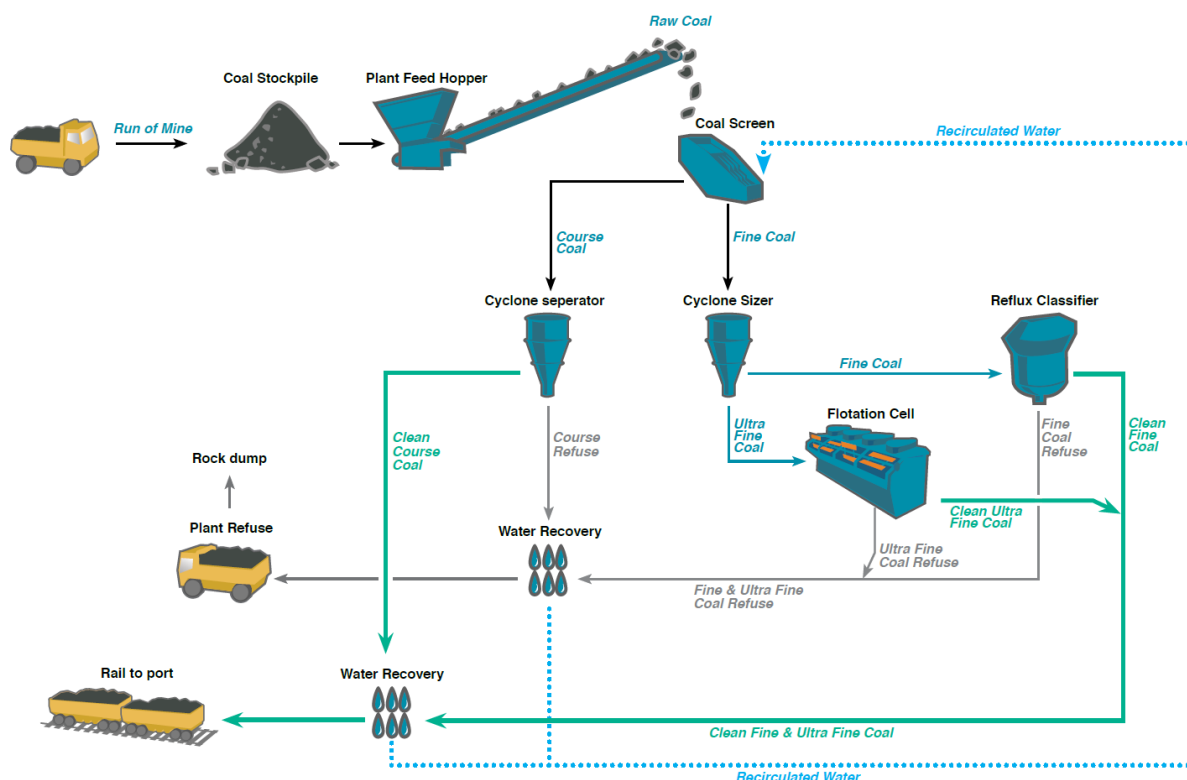


Figure 1 An example of a coal preparation plant including crushing, screening, heavy media and flotation circuits[2]

## 9.2.2 METALLURGICAL PROCESSING

The metallurgical processing of coking coal includes pyrolysis transferring the coking coal to metallurgical coke. The coking coal possible to use varies depending on quality requirements related to the application as well as coke making technology.

## 9.2.2.1 COKEMAKING

In the coal yard the coal is compacted, to avoid oxidation of the coal, and the coal can either be stored in separate piles for each coal type or in a blending pile corresponding to the coal blend for cokemaking. The coal is crushed and in case of separate storage the pulverized coal is mixed in a blending tower.

The coking coal blend is charged into the coke making furnace (example of a density charged furnace in Figure 2) and is heated up in absence of air up to a maximum temperature of approximately 1000-1100°C. In other plants so called stamp charging is used, this means that the coking coal blend is packed before being placed into the coke oven. It is important that the wall pressure is kept below critical values to avoid harming the coke oven, this is especially important with high coke ovens and density charging. When using stamp charging lower quality of the coking coal blend can be accepted and coke with high cold strength can still be produced.

During heating the processes shown in Figure 3 occurs; the coal blend is dried, forms plastic phase while tars and oils are driven off, semi-coke is formed and finally hydrogen is removed. As the coking coal bed is heated from each side the process develops from both sides towards the center during the coking time that is in the range of 17-22 hours. The hot coke is pushed from the oven by a pushing machine via a guide car into the quench car and moved to the quenching tower were the coke is quenched with water. In some plants the coke can be dry quenched by inert gas in a dry cooling plant.
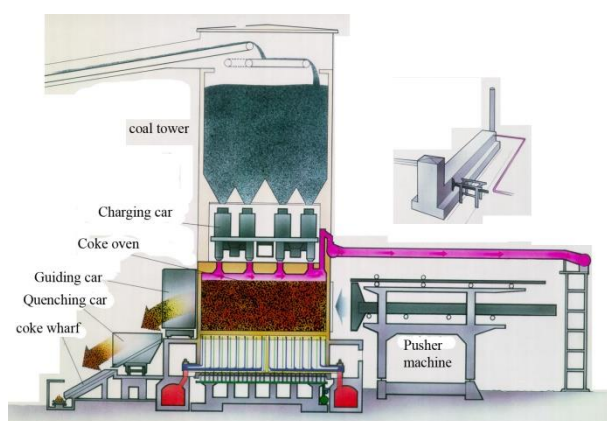


Figure 2 Density charged coking furnace
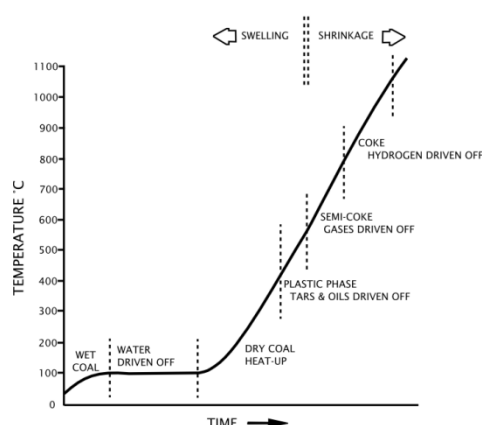


Figure 3 Coke development with temperature[6]

## SUBSTITUTION OF COKING COAL TO OTHER MATERIALS

Lower amounts, e.g. 1-5%, of inert material as e.g. coke dust, thermal coal and petrol coke can to some lower extent be added. Research is on-going in order to increase the possible added amounts of thermal coals to the coal blend, in Japan this was enabled by addition of hypercoal[7-9] to the coal blend. Production of hypercoal involves a first step in which the carbon structure is dissolved into a solvent at elevated temperature and increased pressure. The solid ash is removed and solid carbon precipitated as the solvent is vaporized and collected for repeated use.

## 9.3 VALUE CHAIN, IDENTIFICATION OF SECONDARY RESOURCES AND LOSS OF COKING COAL INTO THE ENVIRONMENT

Secondary resources of coking coal along the value chain are minor regarding types that can be used for coke making. The quality of coking coal needs to be well defined and consistent over time.

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# 10  FLUORSPAR

## 10.1 PRODUCTION LINES OF IDENTIFICATION FROM PRIMARY RESOURCES

Calcium fluoride (Ca F2) is a halide type of mineral, colorful in both visible and UV light. It is widely occurring mineral with significant deposits on over 900 locations. It can occur in vein deposits (together with other minerals with which forms gangue) sometimes associate with galena, sphalerite, barite, quartz and calcite. Is is a common occurrence in minerals of hydrothermal origin and it is a primary mineral in granites and other igneous rocks.

### 10.1.1 WORLD MINE PRODUCTION AND RESERVES

The world reserves are estimated to 260 million tonnes (Mt) with the largest deposits in South Africa (about 41 Mt), Mexico (32 Mt) and China (24 Mt).

China is leading the world production with about 3 Mt annually, followed by Mexico (1 Mt), Mongolia (0.45 Mt), Russia (0.22 Mt), South Africa (0.13 Mt), Spain (0.12 Mt) and Namibia (0.11 Mt).

One of the largest deposits in North America is in the Burin Peninsula, Newfoundland, Canada.

Table 1.  According the USGS, the world mine production and reserves as for 2017 (USG 2007).

| Country | Production – All forms | | Reserves |
|---|---|---|---|
| | 2015 | 2016 | |
| United States | NA | NA | 40 00 |
| China | 4400 | 4200 | 40000 |
| Germany | 40 | 60 | NA |
| Iran | 80 | 80 | 3400 |
| Kazakhstan | 110 | 110 | NA |
| Kenya | 63 | 20 | 5000 |
| Mexico | 1030 | 1000 | 32000 |
| Mongolia | 231 | 230 | 22000 |
| Morocco | 79 | 75 | 580 |
| South Africa | 135 | 180 | 41000 |
| Spain | 98 | 95 | 6000 |
| Thailand | 50 | 50 | NA |
| United Kingdom | 81 | 40 | NA |
| Vietnam | 168 | 170 | NA |
| Other countries | 109 | 89 | 110000 |
| World Total (rounded) | 6670 | 6400 | 260000 |

Besides the mineral resources, fluorspar can be also found in by-production of a number of minerals, among the most important ones is from limestone.
Other sources can be in the mining tailings.
There is also production of synthetic fluorspar, which can be produced from the neutralization of waste in the enrichment of uranium, petroleum alkylation and stainless-steel pickling. However, the further usage can be hindered by slight contamination from the respective production. The Aluminium producers are recycling the HF and the fluorides from smelting operations.

### 10.1.2 MAIN USES

It is used as a flux for smelting and in the production of certain gases and enamels, as well as in the production of hydrofluoric acid. This is an intermediate product for the most fluorine-containing fine chemicals.

## 10.2 REFERENCES

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# 11 GALLIUM (GA)

## 11.1 PRODUCTION LINES OF IDENTIFICATION FROM PRIMARY RESOURCES

### 11.1.1 GALLIUM, PRODUCTION AND APPLICATIONS

Gallium as pure metal is silvery-white in appearance. It is relatively soft metal with a low melting point but with a relatively high boiling point. Gallium is magnetic and a good conductor of both electricity and heat. Due to its properties, it's main use is in GaAs semiconductors in which GaAs acts as a substrate on which one, or more, very thin surface layers are deposited or grown. Depending on the end-uses, different quality substrate crystals are required, with integrated circuits (ICs) and microwave devices requiring the highest. [1]

### 11.1.2 PRIMARY RESOURCES FOR GALLIUM PRODUCTION

#### 11.1.2.1 GALLIUM MINERALS AND ORES

Gallium has an average abundance of 19 ppm in the crustal which is more than some better known metals such as lead or tin. However, it doesn't occur in nature as a native metal but instead it substitutes although in trace quantities for other elements in the minerals. It is generally extracted as a by-product of aluminium or zinc production since it is rarely, if ever, found in significant quantities by itself. There are few minerals in which gallium forms a significant part. Gallite ($CuGaS_2$) is the main gallium-bearing mineral which is similar to the copper sulfide mineral chalcopyrite ($CuFeS_2$). Though the quantities are uneconomic.

Currently, there are no mines working primarily for gallium. However, gallium is recovered as a part a by-product of processing bauxite or sphalerite (ZnS). The gallium in bauxite originates from minerals such as feldspar or nepheline. Weathering processes release both aluminium and gallium from these minerals enriching both of them in bauxite [2]. The average concentration of gallium in bauxite has been estimated to be approximately 50 ppm [3] although it can vary from 10 to 160 ppm [4], [5]. The United States Geological Survey (USGS) reports bauxite reserves of 28 bn t [6]. Based on the average gallium content (50 ppm) in bauxite and its recovery estimate of 40 %, the contained gallium in bauxite amounts to roughly 560 000 t [7]. Around 90 % of the known world bauxite resources are in tropical locations [8]. As for sphalerite, gallium concentrations are known to increase as the temperature of deposition decreases, although it can still be present in intermediate and higher-temperature deposits. Various estimations of gallium content in sphalerite has been reported from 10 up to 366 ppm depending on the continent [9],[10],[11]. The current primary production of gallium is estimated to be about 300 to400 t/a (ROSKILL 2014) which compared to the estimated primary reserves makes the supply secure for several hundreds of years (Figure 4) [7].
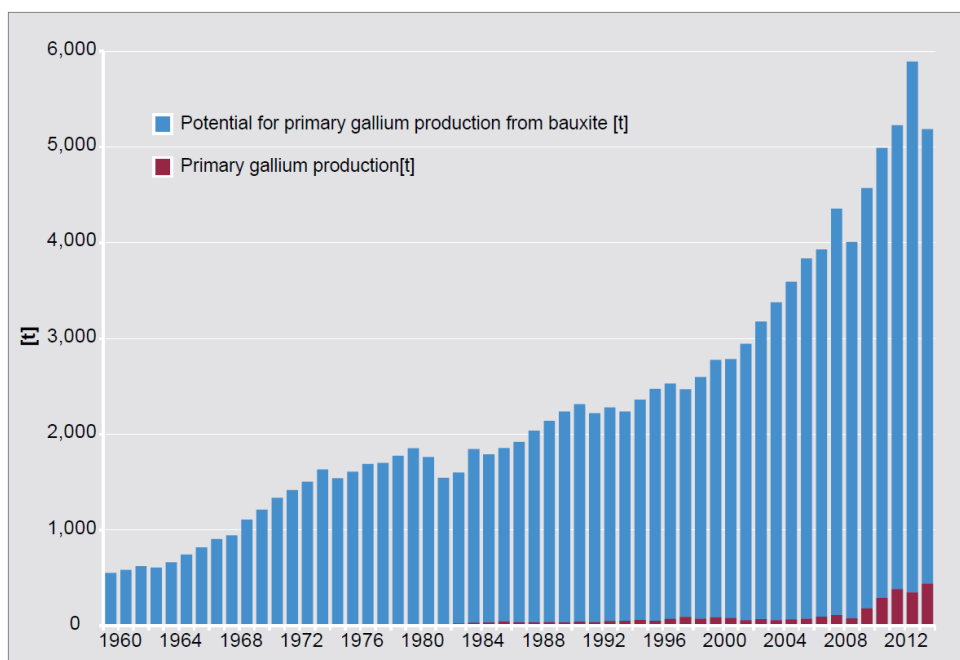
Figure 4. Potential for primary gallium production from Bauxite. [7]

## 11.2 PROCESSING TECHNIQUES RECOGNITION AND ANALYSIS

Processing techniques of Gallium include mineral processing to produce bulk concentrate and metallurgical extraction to gallium and other metals.

### 11.2.1 MINERAL PROCESSING

#### 11.2.1.1 THE GALLIUM BEARING BAUXITE ORE

Most of bauxite occurs close to the surface, with only 1 or 2 m of overburden. Typical deposits range in thickness from 3 to 15 m. The majority of the bauxite is mined and processed without beneficiation. Some exceptions exists, for example in the north of Brazil and in Vietnam the high clay content requires a washing process before further processing. [8] Typical processes involved in the mining of surface deposits are: [8]

- Clearing of vegetation and collection of valuable topsoil using scrapers and bulldozers.
- Removal of overburden.
- Blasting or ripping of some parts of the ore that cannot be dug easily. This involves drilling and placing explosives, or ripping with large bulldozers.
- Loading onto trucks and hauling to a crushing facility. Trucks ranging in size from 30 to 180 tonnes are used in different size mines.
- Landscaping and rehabilitating back to the existing land use in collaboration with the local people and government.
- Crushing and sorting.
- Washing and beneficiation (further treatment of the ore to concentrate the minerals) if necessary.
- Delivery to export or to local refineries.

## 11.2.1.2    THE GALLIUM BEARING ZINC ORES

In general, beneficiation of zinc ores compose of processes such as: crushing, milling, sizing, flotation, filtration, thickening, gravity concentration. Currently, due to the developments in selective reagents and advancements in grinding techniques, flotation has virtually replaced gravity concentration. However, gravity concentration can still be used for preconcentrating before fine grinding and flotation. Selective flotation may be used if the ore composes of complex sulphide minerals. Within this different ores are selectively separated in different flotation circuits. An example of lead-zinc flotation is presented in Figure 5.
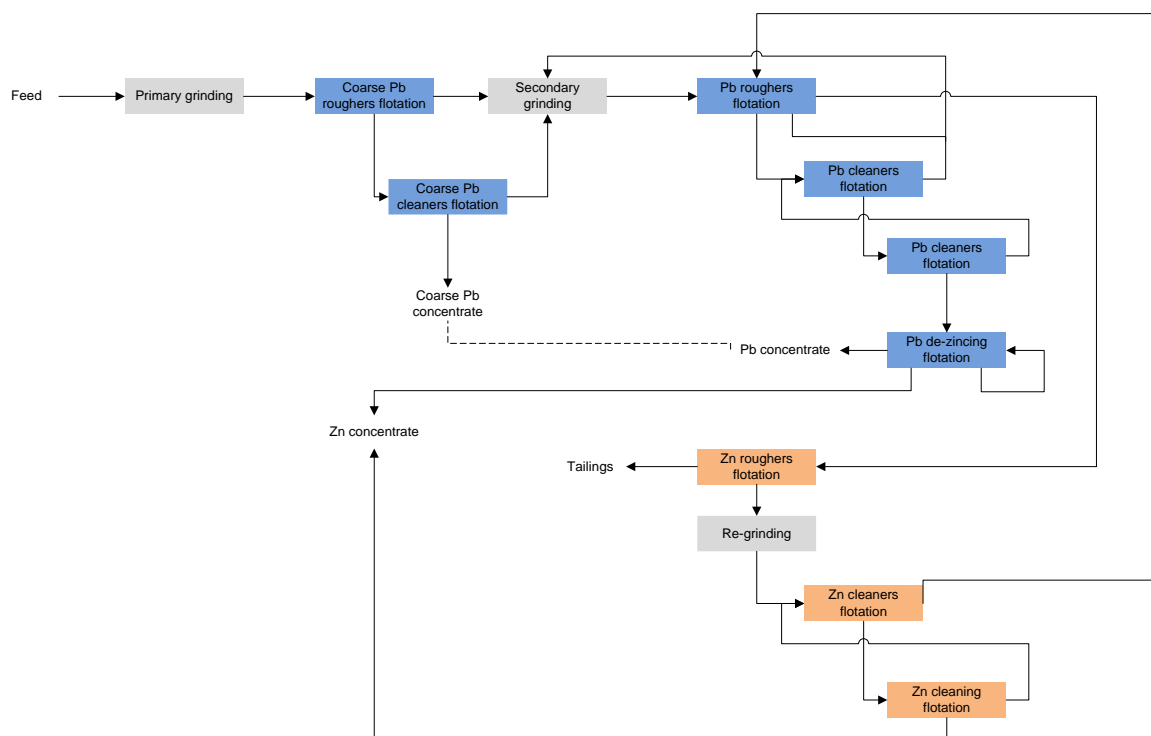


Figure 5. An example beneficiation process for lead-finc bearing ore. [12]

Typically in the feed, zinc content varies between 1 % and 10 %. After beneficiation, the zinc concentrate grade is 50-60 %. Gallium follows zinc to the zinc concentrate and further to the zinc extraction.

## 11.2.2 METALLURGICAL EXTRACTION

## 11.2.2.1    GALLIUM EXTRACTION FROM BAUXITE AND ZINC ORES

Roughly 90 % of current primary gallium production is extracted from bauxite during the refining of alumina (Figure 6). The most common process for the alumina production from bauxite and thus gallium is Bayer process. In this process aluminium bearing minerals in bauxite are selectively extracted from insoluble components by dissolving them in a solution of sodium hydroxide (caustic soda) at high temperature and high pressure. The "Bayer liquor" solution contains sodium aluminate and non-dissolved bauxite residue containing iron, silicon, titanium, aluminium, and other elements in small quantities, including gallium. [7] This solution with an equilibrium concentrations of 100-125 ppm of gallium is then recycled on a continuous basis [1]. In the

Bayer process roughly 70% of the gallium is leached into the caustic soda solution, and the remaining 30% is disposed with the red mud [13].

The recovery or gallium from sodium aluminate solutions is carried out by various methods such as fractional precipitation, electrochemical deposition, solvent extraction, and ion exchange. Currently, ion exchange is the main method applied in the industry (Figure 7). These proprietary techniques utilize different type of ion exchange resins to extract the gallium from the liquor. Beside the type of resin used, also their longevity and the purity of the Bayer liquor have an important bearing on the cost of extracting the gallium from the liquor. Extraneous and/or unexpected impurities in the liquor can drastically reduce the life of resins and drive up the cost. Solvent extraction could be an efficient method to extract gallium from Bayer liquor, however its kinetics has been proved to be very slow, generally requiring several hours. [1], [7]

A small amount of gallium is produced also as by-product of zinc extraction from sphalerite ore (ZnS) (Figure 6). During this process the sphalerite is first roasted to zinc oxide (ZnO) and then leached with sulphuric acid. Gallium is contained in impurities which are separated from the leach solution by the addition of antimony trioxide, zinc dust or proprietary reagents. The gallium is then extracted from the resulting separated solids or 'cement residues'.[1]

Finally, during the production of alumina as well as refining of zinc, electrowinning is used to create a crude gallium metal at purities of 99.9 to 99.99 % (3N/4N gallium). In order to meet highest purity requirements (7N gallium 99.99999 %) typically fractional crystallization and zone refining is utlized. [7]
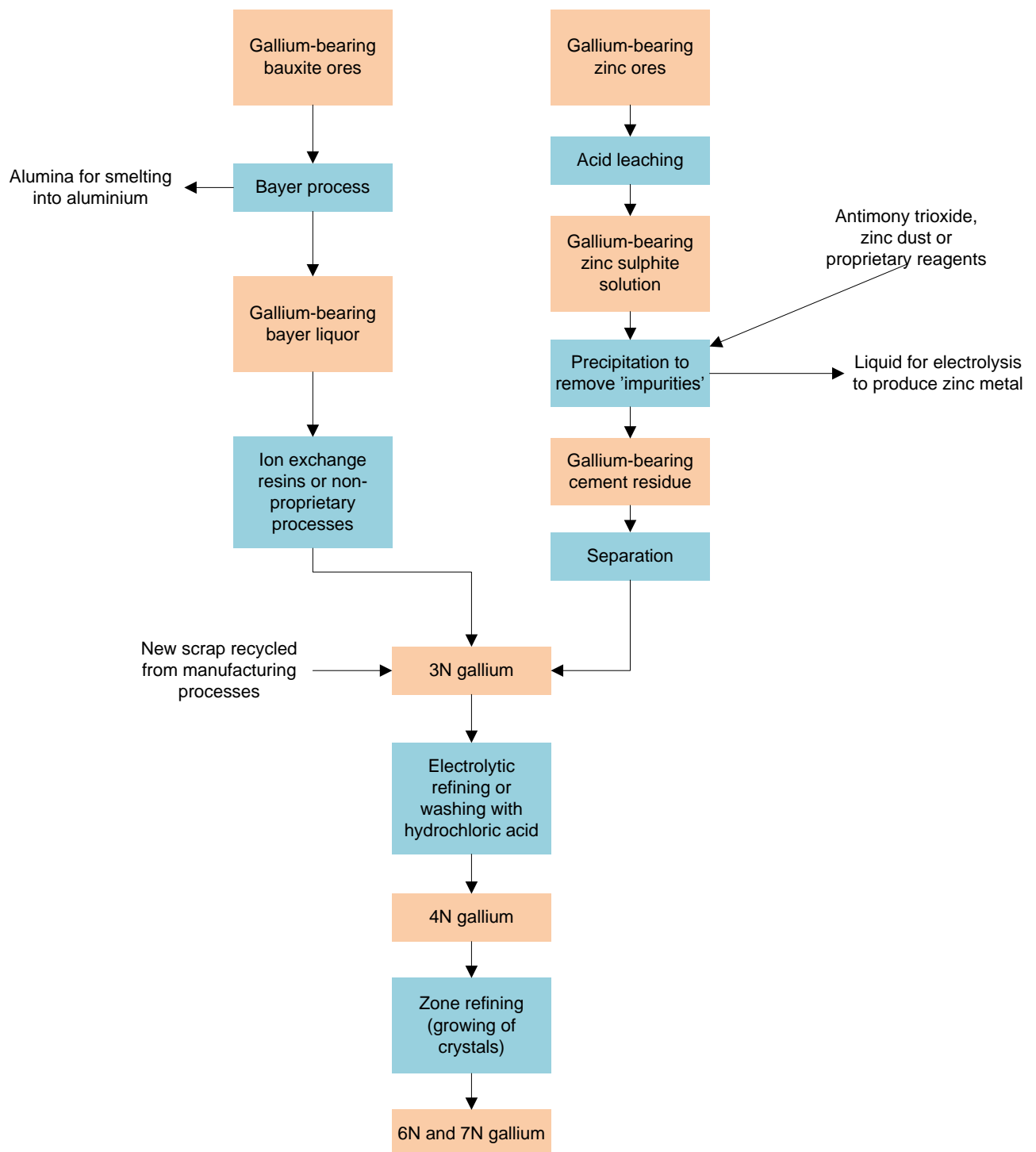
Figure 6. Process to extract gallium from bauxite or zinc ores. [1]
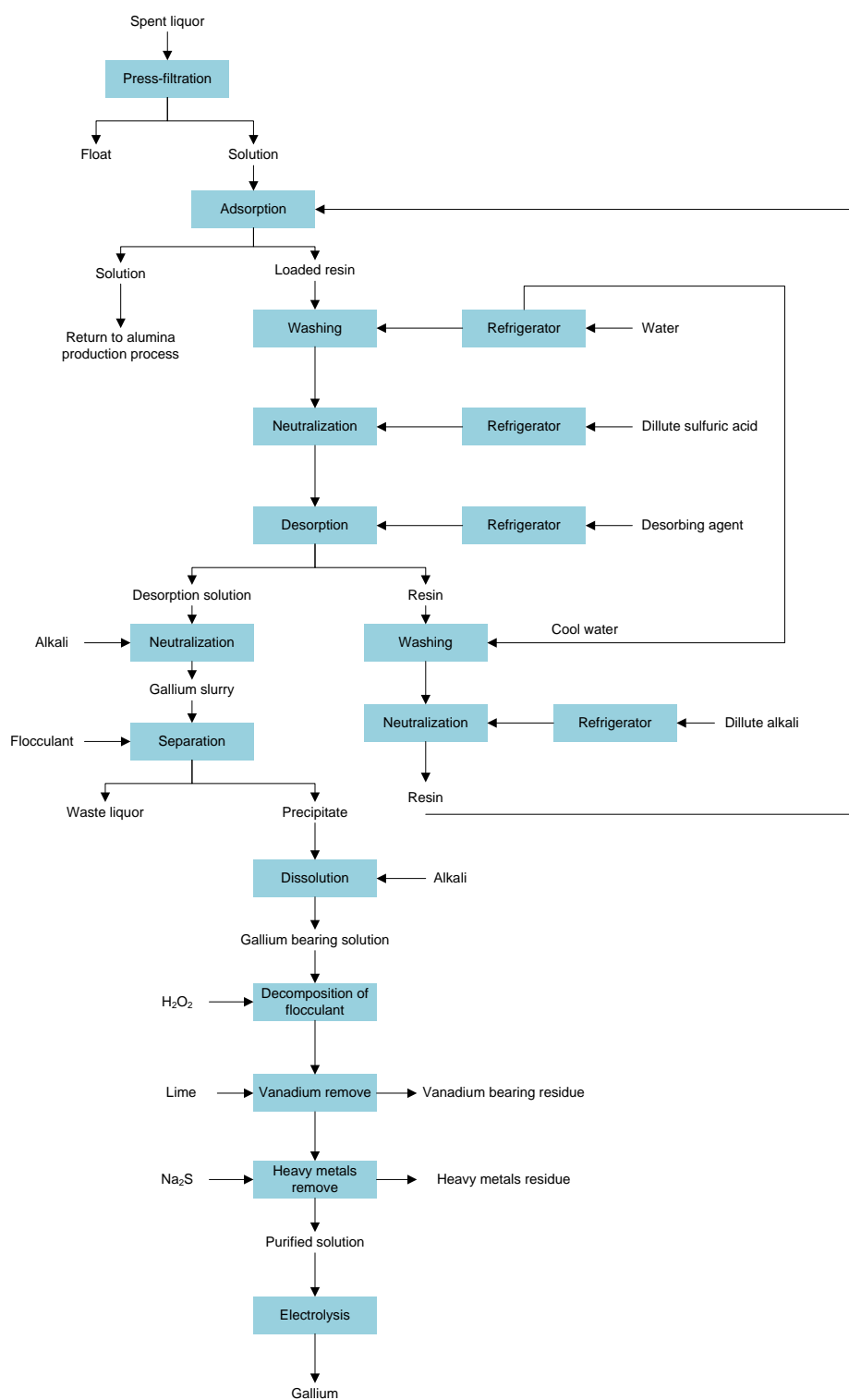
Figure 7. Flow sheet of an ion exchange method. Derived from. [13]

## 11.2.2.2    OVERALL PRODUCTION OF GALLIUM

Reliable data for production and capacity of refined gallium are very difficult to obtain and in many cases, it is impossible to differentiate whether production is derived from secondary gallium or upgraded 3N/4N gallium.

According to estimates of the USGS, refined high grade gallium production in 2016 was about 180 t which present rough 56 % of the refinery capacity (320 t) in 2016. Further on only 48 % of the primary gallium production of 375 t was refined. The global primary low-grade gallium production capacity in 2016 has been estimated to be 730 tons per year. [14] During the past years, the production has been usually below 50 % of the capacities, rarely above (Figure 8). Solely during a short period between 2010 and 2012 there was an increase in the utilization capacity which varied between 70 to 80 % [7].
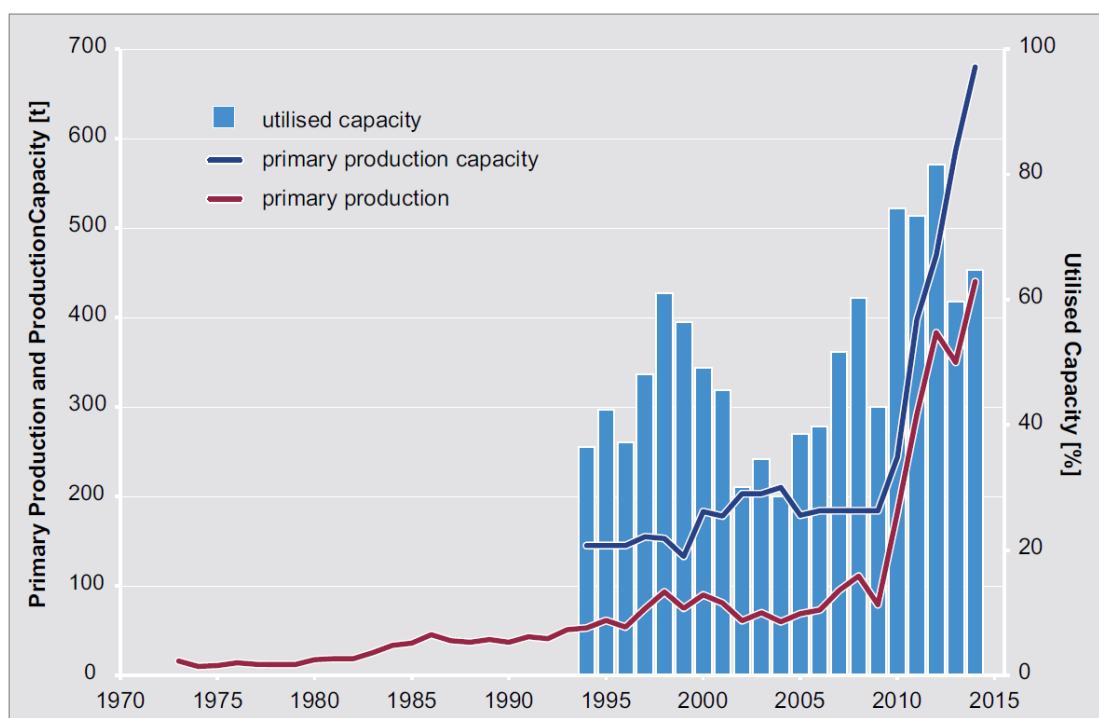


Figure 8. Production, production capacity and utilization capacity of low-grade gallium. [7]

Few studies of the global gallium substance flow in 2011 has been carried out [15], [16] which can be seen in Figure 9 and Figure 10.
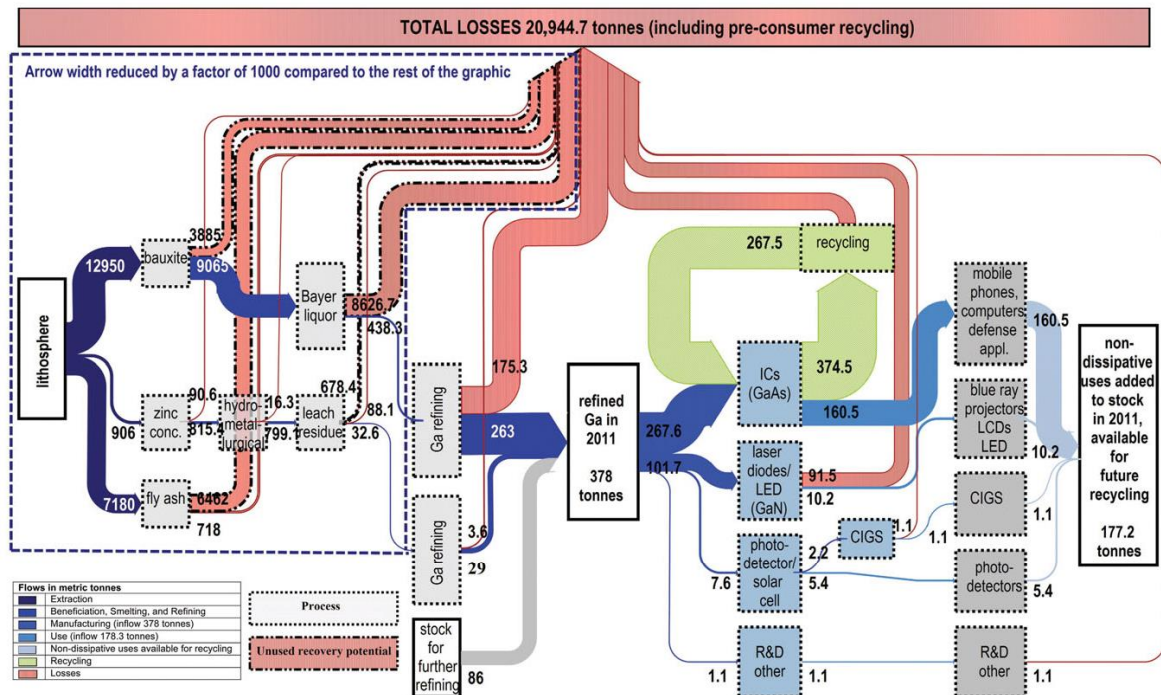
Figure 9. Global gallium flow analysis in 2011. zinc.con.=zinc concentration; Ga=gallium ; ICs=Integrated circuits ; GaAs=gallium arsenide ; LED=light-emitting diode ; GaN=gallium nitride ; R&D=research and development; GICS=copper indium gallium diselenide; LCDs= liquid crystal display. Note the scale difference in the box of dashed line. [15]

**Global anthropogenic gallium system 2011 [tons/year]**
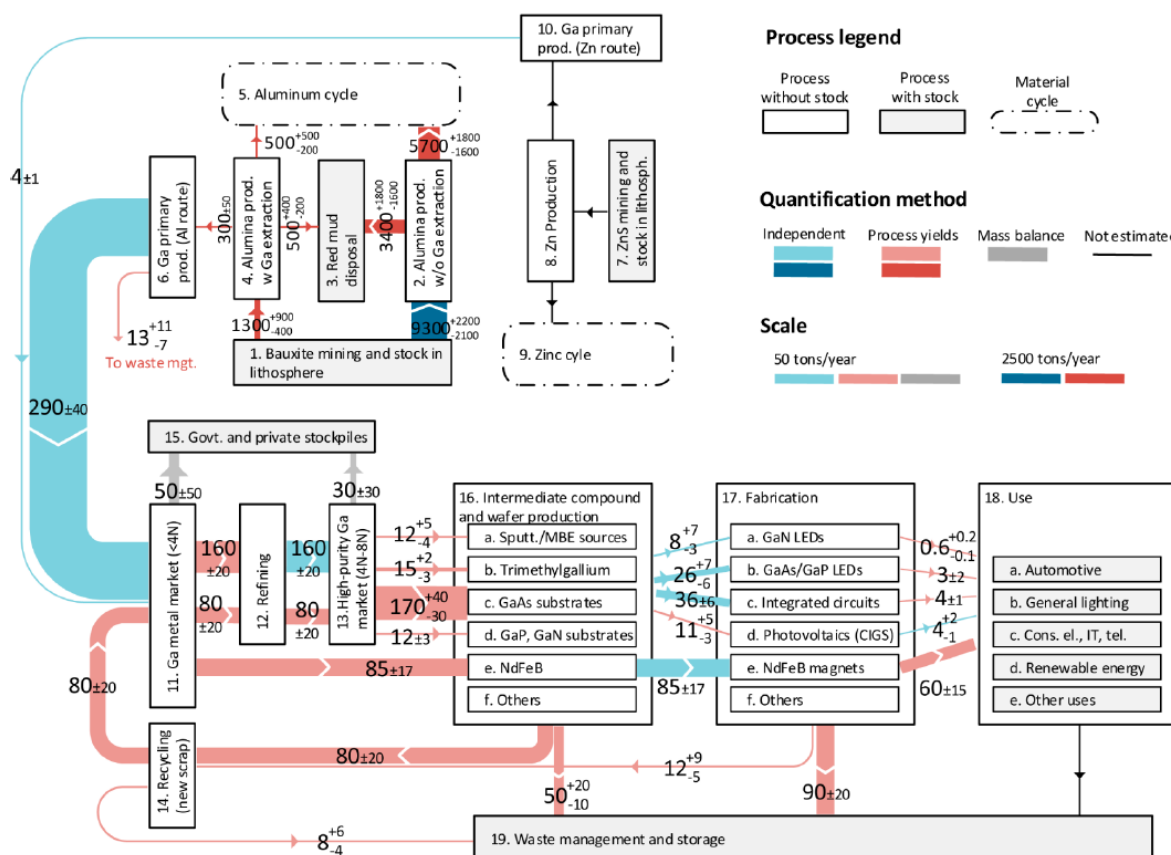
Figure 10. Global system of gallium production, refining, fabrication, use and recycling. Quantified flows are given as median ±84th and 16th percentile of Monte Carlo simulation. Colors indicate quantification method. Note that the flows in the upper part (dark colors) are shown in a different scale.[16]

From Figure 9 and Figure 10 it can be seen that major source for gallium is the bauxite ore, however it should be noticed that a significant share of gallium do not end in gallium refining but ends up in the residue (red mud) or in the aluminum cycle. This is owing, in great extent, to the fact that only few aluminum production companies have gallium extraction facilities which leads to loss of gallium in larger perspective [15]. As a result, there is significant margin for gallium optimization at the beneficiation/ smelting/refining and manufacturing levels.

Main producers of primary gallium with their estimated production capacities in 2014 has been presented in Table 2.

Table 2. Estimated global annual primary gallium production capacity 2014. [17]

| Country | Capacity (t) |
|---|---|
| China | 551 |
| Germany | 40 |
| Hungary | 8 |
| Japan | 10 |
| Kazakhstan | 25 |

| Korea, Republic of | 16 |
| Russia | 10 |
| Ukraine | 15 |
| **Total** | **675** |

## 11.2.2.3    GLOBAL INDUSTRIAL ACTORS

Major global industrial actors in gallium extraction from primary raw materials are [7]:

**China**

- *Zhuhai SEZ Fangyuan Inc.*, is China's and the world's largest producer of primary gallium. It accounts with a capacity of 140 t per year at six locations for more than 30 % of total world output. The company produces 4N and 6N gallium and is owner of a patent of a chelating resign for adsorbing gallium

- *Aluminium Corporation of China Ltd.* produces gallium metal and gallium oxide at four sites at Shandong, Henan, Guizhou and Shanxi province. In 2014 the company produced 81.2 t of gallium, after 127.8 t in 2013 and 39.2 t in 2012.

- *East Hope Mianchi Gallium Industry* at Mianchi County, Henan Province ranks third with a capacity of 80 t/a and a production of 40 t/a.

- *Shanxi Jiahua Tianhe Electronic Materials* is a joint venture of Molycorp, Shanxi Aluminium Plant and Beijing JiYa Semiconductor Material. Its capacity is estimated at 50 t/a

- *Xiaoyi Xingan Gallium Co., Ltd* was founded 2011 by Xiaoyi Xingan Chemials Co. Ltd, a subsidiary of Hangzhou Jinjiang Group, one of the major alumina and aluminium producers in China. (50 t/a). The company reports a capacity for the production of 4N gallium of 50 t/a and has the world's largest single production line.

- *Beijing JiYa Semiconductor Material Co.* is a joint venture of the US company AXT Inc., Consco Group, Hong Kong and Shanxi Aluminum Plant and has a capacity of 45 t/a.

- *Shanxi Zhaofeng Gallium Industry Co.* is a joint venture of Shanxi Zhaofeng Aluminum Co., Ltd of Yangmei Group, Beijing JiYa Semiconductor Material Co., and Chalco Jinlv Refr Co. It has a capacity of 20 – 40 t/a.

- *Nanjing Jinmei Gallium Co., Ltd.*, a joint venture between the US company AXT Inc. (83 %) and Nanjing Germanium Factory (17 %). On its website the company reports capacities for the production of 100 t of high-pure gallium of 5N to 8N, including MBE gallium, of 50 t for crude gallium from recycling, of 6 t for 4N/5N gallium oxide, and of 2 t for 4N/5N gallium nitride.

- *MCP Metals (Shenzen)*, owned by 5N Plus, Canada. A joint venture called MCP Crystal was formed in 2009 between the MCP Group and the Chinese company Golden Harvest Ltd. to create an integrated gallium operation capable of producing both low-purity and high-purity gallium. The joint venture consisted of four operations, three 99.99 % (4N) plants and one 6N and 7N plant.

The 4N plants were expected to collectively produce between 70 t/a and 80 t/a of gallium. The plants were located in Henan, Shangxi, and Sichuan Province.

- *Vital Materials Co.* produces high purity gallium (5N – 7N). The joint venture operation with Hangzhou Jinjiang Group will produce 60 t/a. Crude gallium is supplied by Jinjiang's subsidiary Xingan Gallium. In addition to gallium metal, Vital produces gallium compounds like gallium oxide, chloride, sulfate, nitrate, phosphide, antimonide and trimethyl gallium and recycles gallium from gallium- bearing scrap.

- *Emei Semiconductor Material Factory & Institute* is according to its company profile the biggest producing center for high pure elements and compound materials in China. The company was founded in 1964 and is situated in Leshan, Sichuan province. The company produces and sells a wide range of high purity elements including gallium of 5N – 7N.

- *Sichuan Western Minmetals Co., Ltd.* is a supplier providing a wide range of high purity metals and oxides including gallium metal of 5N – >7N and gallium oxide and gallium trioxide of 4N – 5N. The company is headquartered at Chengdu, Sichuan province

- *Sumika Electronic Materials (Shanghai)* was established as a 70/30 joint venture named Shanghai Sumika High Purity Metal Ltd. in 2001 by Sumitomo Chemicals Co. Ltd and Inabata & Co., Ltd, Japan. The refining facility has a capacity of 40 t/a of 6N – 7N gallium metal, which will be supplied to Sumitomo.

- Zhuzhou Keneng New Material Co., Ltd. was established in 2001 at Zhuzhou, Henan privince. The main products include indium, bismuth, tellurium, and 4N and 6N gallium.

**Germany**

- *Ingal Stade GmbH*, based in Stade near Hamburg which extracts annually about 30 t of primary gallium from Bayer process liquor of the alumina refinery.  For further treatment and refining up to 7N purity the gallium is shipped to the owners' facilities in the UK and the USA.

- *PPM Pure Metals GmbH* at Langelsheim has a very long tradition in the production and refining of high purity metals and compounds. PPM is engaged in the production of high purity minor metals and their compounds for mainly the electronic, opto-electronic, and photovoltaic industries. This includes ultra pure metals (up to 7N5 quality) and compounds of the elements antimony, arsenic, cadmium, copper, gallium, germanium, indium, lead, tellurium, and tin. PPM produces gallium from 4N – 8N purity by recycling scraps, residues and slurries from gallium arsenide pulling, wafer and epitaxial processing, and other gallium containing materials. The estimated capacity of PPM is around 10 t/a.

**Hungary**

- *Magyar Aluminium Zrt. (MAL)* is situated in Ajka 150 km west of Budabest and operates an alumina facility processing domestic and Bosnian ores. MAL extracts crude gallium from Bayer liquor with a purity of 4N to 7N. The capacity has been estimated to be around 8 t per year.  The

last reported production was 3.9 t in 2009. According to company reports gallium production stopped in 2013.

**Japan**

- Japan has a production capacity of primary gallium of about 10 tons per year. It is recovered from the by-products of the zinc smelting process of *Akita Zinc Co., Ltd, Iijima Smelting Plant*, an 81 % subsidiary of *DOWA Metals and Mining Co., Ltd.*

- *Dowa Electronic Materials Co., Ltd* refi nes gallium that is produced from by-products of the zinc smelting process at Akita Zinc Co's Iijima Smelting Plant and from recycled gallium scrap to purities up to 7N. Capacity is estimated at 90 t/a. By its own account the company holds the no. 1 share in sales of high purity gallium in the world market. Dowa Electronics also supplies gallium oxide, gallium arsenide and gallium nitride based epitaxial wafers and LEDs.

- *Sumitomo Chemicals Co.* is a major Japanese chemical company and a member of the Sumitomo Group. The company has high purity gallium capacities of about 100 t/a of which 60 t are at Ehime plant, Japan, and 40 t provided by Sumika Electronic Materials (Shanghai). Sumitomo Chemical's gallium products include high purity gallium, trimethy gallium, triethyl gallium, and gallium arsenide wafers.

- *Rasa Industries, Ltd.* started as Rasa Island Phosphate Ore Co., Ltd. in 1911. The production of high purity gallium from semiconductor wafer scrap began 1982 at Osaka factory. Rasa's Electronic Materials Sector is engaged in the manufacturing and sale of high purity inorganic materials, including gallium of 6N/7N purity. Estimated upgrading and refining capacities are 35 t/a.

- *Nippon Rare Metal, INC.* (NRM) started in 1958 as a supplier of selenium, photoelectric cells and metal salts. In 2000, the company began with the recovery of gallium and tantalum. It produces 4N – 5N gallium and gallium oxide from wafer production scrap and copper-indium-gallium-selenium (ICGS) scrap from thin film solar sector. Estimated upgrading and refining capacities are10 t/a.

- *The Nichia Corporation*, headquartered in Tokushima is one of the world's largest producer of gallium compound based LEDs with distribution offices around the world. Estimated upgrading nd refining capacities of high purity gallium are 15 t/a.

**Kazakhstan**

- Kazakhstan has an annual production capacity of crude gallium of 20 – 22 t. Aluminium of Kazakhstan (AoK), a subsidiary of the internationally operating mining company *Eurasian Natural Resources Corporation PLC (ENRC)*, is extracting about 5 Mio. t of bauxite per year in the region of Pavlodar in the northeast of Kazakhstan. Production of alumina amounts to 1.5 Mio. t. In the process gallium is recovered as a by-product. From 2008 to 2011 there was an annual primary gallium output of about 18.7 t. In 2012, the production decreased to 15.7 t, and since 2013 ENRC has stopped the production of gallium completely.

**Russia**

- The primary gallium production capacities of Russia are estimated at 12 t/a. *OAO Pikalevskii glinozem (Pikalevo Alumina)* which operates as a subsidiary of LLC BaselCement produces gallium from apatite nepheline ore. *OOO Gallii (Gallium)* at Kamensk-Ural produced gallium from bauxites. The company has a capacity of 4 t/a but stopped production in 2012

**Slovakia**

- Until 2009 the USGS reported capacities for the production of primary gallium of about 8 t/a for Slovakia, but since 2010 there is no production of primary gallium in Slovakia

- *CMK, s.r.o.* based in Zarnovica was founded in the 1970's as a research institution. The company's portfolio covers gallium arsenide wafers and gallium metal of 4N, 6N, and 7N purity. The gallium is refi ned from low purity primary gallium (3N, 4N) and from recycled waste material containing gallium (gallium arsenide, chloride, oxide). Current capacity and production data are not available, the last reported data where recycling and refining capacities of 25 t/a for the years 2006 – 2009 and a production between 16.75 t (2006) and 6.05 t (2009)

**South Korea**

- *Korea Zinc Co., Ltd*. began producing 6N primary gallium as a by-product of its zinc smelting operation at Onsan in the fi rst quarter of 2010 with an estimated annual capacity of 10 t. After several facility expansions between 2010 and 2012 the current capacity is estimated to be between 16 and 20 t/a.

**Ukraine**

- The Ukraine has estimated primary gallium production capacities of about 15 t/a. The gallium at purities of 99.99 % and 99.999 % is produced at the Nikolaev Alumina refinery owned by *United Company RUSAL Plc (RUSAL)*, which refines bauxite imported from Guyana and Guinea.

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## 11.3 TECHNICAL INNOVATIONS IN GA PRODUCTIONS FROM PRIMARY RESOURCES

### 11.3.1 MINERAL PROCESSING

#### 11.3.1.1 ORE ECONOMIC AND ENVIRONMENTALLY FRIENDLY METHODS

**Economic**

As it has been stated previously, gallium-bearing minerals do not form solely economically recoverable concentrations. When it comes to the current practice of gallium production as a by product of mainly alumina production from bauxite, economical challenges has been reported to occur. For example, impurities in the Bayer liquor may increase the use of the resins in the gallium ion-exchange extraction and therefore drive up the costs [1]. As a result the gallium extraction costs are linked to the aluminium Bayer process and further on the Bauxite composition.

Regarding the supply side, gallium production is price sensitive and potentially more by-product gallium can be supplied from alumina refineries with appropriate investment should the price rise. Currently there is a large amount of overcapacity in gallium markets. (CRM list, material profiles 2014)

**Environmentally**

Significant quantities of waste, called red mud, is produced in the aluminium processing. It has been estimated that around 120 million tonnes of red mud is produced annually around the world. In addition, the bauxite residue disposal areas contain an estimated 2.7 billion tonnes of this hazardous classified waste. [18] Discharge of red mud is damaging to the environment due to its high alkalinity, numerous heavy metals and tiny amount of radioactive elements [19] Therefore, it has been stated to be one of the most important disposal problems in the mining and metallurgy industry.

As described in the global gallium flow analysis (Figure 9 and Figure 10), only a small share of gallium ends in refining and in use which generate losses and inefficient recovery.

Within the recovery stage of gallium, one alternative method to recover gallium from sodium aluminate solutions is mercury cathode electrolysis. In this method liquid mercury acts as a cathode allowing possible precipitation gallium during the electrolysis. Rather large amount of mercury must be kept in the circulation to isolate relatively small quantities of gallium or to react such small quantities of gallium with sodium. Due to the use of high toxicity of mercury, and it has been prohibited for use in most countries. However, some single facilities still exist. [13]

Recently, a renewed interested in the use of gravity concentration in recovering PGMs is being studied due to the economic importance and new available gravity concentration devices [5][26]. Further, the flash flotation is more attractive application due to the capability of quickly lowing circulating load and relatively low cost of installing a flash unit [27].

## 11.3.2 METALLURGICAL EXTRACTION

### 11.3.2.1    FASTER, SIMPLER AND MORE EFFICIENT REFINING METHODS

As was stated in previous section  gallium is extracted and recovered as a by product of mainly alumina production from bauxite. Therefore, gallium production is linked to the primary alumina production. In addition, only few aluminium producers have gallium extraction facilities partly due to the fact that the additional processing disturbs the closed-loop recycling process of the Bayer liquor in the alumina production [13]. Due to the low grade of gallium as a gallium-bearing mineral, makes mining and beneficiation targeted on primarily gallium-bearing minerals un economic and unfeasible.

During the gallium refining and recovery from Bayer liquor, co-extration of vanadium in the ion-exchange create problems by building up in the resin and therefore reducing the loading of gallium. Simultaneously, vanadium build-up give rise to a serious operational problem. At the moment proposed solutions to solve the problem such as shortening the contact time and scrubbing with concentrated sodium hydroxide would also cause the decrease of gallium recovery and other side effects. Another reported problem in the ion-exchange, due to the strong acid media, is the degradation of amidoxime groups (resin) to hydroxamic acid which cannot extract gallium from Bayer liquor but is known to extract copper. Consequently further investigation is needed

to solve these problems. One further research topic could be the recovery of relatively valuable vanadium prior to the gallium which would solve the problem of vanadium co-extraction. [13]

Isocratic elution chromatography does potentially offer refiners greater simplicity in the form of a unit process. Much research and development in the field of polymer supports has taken place over the latter half of the century albeit mostly for the rapidly growing biological separations industry [16].

## 11.4 CHARACTERIZATION OF MINING TAILINGS AND PROCESSING RESIDUES AND POTENTIAL UTILIZATIONS

The overall elemental gallium studies have identified significant quantities of gallium ending to residues and tailings in the current extraction of gallium from Bauxite due to the significant margin for gallium optimization at the beneficiation/ smelting/refining and manufacturing levels [15], [16]. The quantified losses to the residues have been reported to represent 70 times the amount of gallium potentially available from end-of-life recycling. In 2011 the estimated amount of gallium ending to red mud globally has been assessed to be roughly 3 885 tons. Other identified sources could be aluminous claystone and mudstone. [15]

### 11.4.1 CHEMICAL AND MINERALOGICAL CHARACTERIZATIONS

Red mud has been identified as a possible source for gallium. Red mud composes mostly form aluminium, iron, silica and materials (such as calcium and alkali) which has been added during the refining. Beside gallium other trace elements such as scandium, yttrium, vanadium, chromium, uranium, thorium and REE's has been identified to exist in red mud. [20] In Table 2 the chemical composition of red mud is presented.

Table 3. The chemical content of red mud. [20]

| Major element | Concentration (%) |
|---|---|
| Fe | 4.52 - 50.6 |
| Al | 4.42 - 16.06 |
| Si | 2.16 - 14.86 |
| Na | 0.98 - 7.79 |
| Ca | 0.39 -  16.72 |
| Ti | 0.98 - 5.34 |
| Minor element | Concentration (mg/kg) |
| U | 50 - 60 |
| Ga | 60 - 89 |
| V | 730 |
| Zr | 1230 |
| Sc | 54 - 120 |
| Cr | 497 |
| Mn | 85 |
| Y | 60 - 150 |
| Ni | 31 |
| Zn | 20 |
| Lanthanides | 0.1% - 1% |
| Th | 20 - 30 |

## 11.4.2 POTENTIAL UTILIZATION

Currently there is no or very limited commercial operation for gallium recovery from red mud. However, Orbite Technologies Inc have been developing a process to treat i.a. red mud and planning to start operation in near future. In Figure 7 a schematic description of the Orbite process for red mud has been presented.
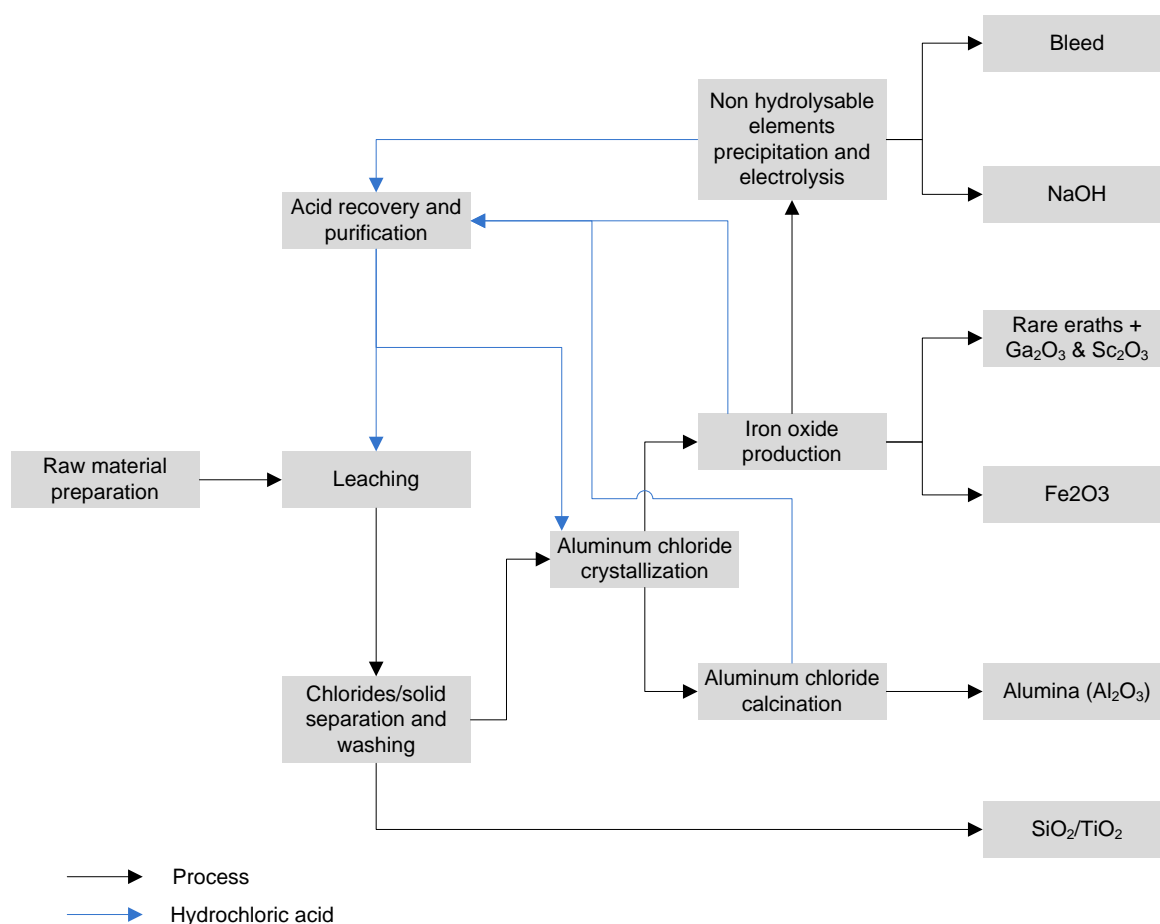


Figure 11. Overall process of Orbite for secondary raw materials such as Red mud to recover i.a. Gallium. [21]

The process has been developed to treat also other feeds such as aluminous clays and tailings to recover valuable elements including gallium.

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## 12 GERMANIUM

### 12.1 PRODUCTION LINES OF IDENTIFICATION FROM PRIMARY RESOURCES

Germanium is enlisted into the group of strategic raw materials for its limited production volume (160-165 tpa in 2016, including outputs from primary (~70%) and secondary (~30%) sources), dominated by China [**USGS, 2017**]. This factor makes the market prices highly volatile and destabilizes the supply/demand equilibrium, important for the main germanium application sectors.

The main germanium application fields are as a metal in infrared optics and electronics, as $GeO_2$ in PET production catalyst and as $GeCl_4$ in optic fibres production. Germanium is produced only as a accoupling metal. It is a by-product recovered from flue dusts generated during zinc and copper-zinc smelting and coal fly-ash.

### 12.2 PROCESSING TECHNIQUES RECOGNITION AND ANALYSIS

#### 12.2.1 MINERAL PROCESSING

Germanium is a rare element, which Earth crustal abundance is estimated at 1.5 ppm for oceanic and 1.6 ppm for continental crusts. The average Ge content in the Earth is 13.8 ppm, with

37 ppm in the core and 1.1 ppm in primitive mantle – Ge is present in trace quantities in almost all rock types, due to its siderophile, lithophile, chalcophile and organophile character. Germanium concentration in water ranges from 0.06 ppb on river waters to several 100 ppb in thermal waters.

Ge does not occur in nature in elemental form, but it creates about 30 known germanium minerals, mainly of sulphidic character [**Melcher, Buchholz, 2014**]. The most known germanium minerals are: renierite – $(Cu,Zn)_{11}Fe_2(Ge,As)_2S_{16}$; briarite – $Cu_2(Fe,Zn)GeS_4$, that both could be found in Kipushi deposit (DRC); germanite - $Cu_{13}Fe_2Ge_2S_{16}$, present in Tsumeb deposit (Namibia), and argyrodite – $Ag8GeS6$, found in Freiberg (BRD). These germanium minerals nowhere create economically mineable aggregates, being scattered in their surroundings.

Germanium production volume for 2016 has been assessed as 155-160 tones [**USGS, 2017**], of which 70% derived from primary sources, and the rest from recycling materials. The principal germanium producing country is China, with output of about 110 tpa, which means almost 70% share, the minor producers being: Russia (~5 tpa), USA ($3 \div 5$ tpa) and others, such as: Belgium, Canada, Germany, Ukraine, with combined germanium volume produced of about 40 tpa.

Germanium manufacturing from primary raw materials is supported by such fed material streams as: coal fly ashes (with share of 56%), zinc manufacturing residues (with share of 33%) and other base materials processing byproducts (with share of 11%) [**Verhelle, 2014**].

#### 12.2.2 METALLURGICAL EXTRACTION

Ge primary raw materials suitable for germanium recovery usually contain from 0.1 up to few percent of germanium, with matrix compositions dependent upon their origin. Therefore, their preliminary processing in individual cases are different, adapted to the character of raw material and technical and technological resources being at disposal.

For initial upgrading and enrichment of primary raw materials the pyro- and hydrometallurgical methods are applied. The pyrometallurgical methods depend on heat treatment of charge under reducing conditions, with or without reoxidation of resulting dusts and fumes, where Ge creates the forms of GeS, GeO2 or GeO. These dusts and fumes, depending on their matrix and Ge content may be further treated on the hydrometallurgical route, either by applying directly HCl + Cl2 gas leaching, with crude liquid GeCl4 recovery, or using conventional leaching procedures. This conventional leaching may be also applied as the first operation for direct treatment of Ge – bearing primary raw materials. In most cases, leaching is performed with H2SO4 solutions, sometimes with addition of reducing or oxidizing agents. Resulting sulphate leach solutions are further treated for separation of germanium in the form of solid or liquid Ge concentrates. To obtain Ge solid state concentrates the precipitation methods are used, with germanium recovery as: GeS2 (reagents: H2S or Na2S); GeO2 or divalent metal germanate (reagents: NaOH, Na2CO3, MgCO3); germanium cement (reagents: metallic Zn or Fe), or Ge – tannin complex (reagent: tannic acid), while Ge liquid concentrates may be obtained using solvent extraction (SX) or ion – exchange (IX) techniques, resulting in better purified and more concentrated Ge solutions, suitable for precipitation of enriched solid Ge concentrates. The conventional methods of Ge precipitation from leach solutions (as: germanium sulphide, oxide, germinate or cements) do not need to be elucidated, being simple and easy to perform.

The tannin method, discovered by Schoeller in 1932, is often applied, especially for Ge precipitation from zinc residues leach sulphate solutions (H2SO4 – Zn2+ - Fe2+/3+), with Ge content < 1 g/l, and depends on creating insoluble Ge – tannin complex using polyhydroxycarboxylic acids, such as tannic acid. For effective and to some extend selective Ge precipitation the following conditions should be maintained [Liang, 2008], [Bayat, 2016], [Anderson, 2015]:

- iron present in divalent form;

- pH in the range of 1.5 ÷ 3,0;

- temperature preferable high (e.g. 60 ÷ 90 ºC);

- reaction duration up to 5 hours;

- dose of tannic acid in great excess versus present in the solution, introduced in a few portions (to be established experimentally).

In optimized conditions the germanium precipitation rate may reach over 95%, and obtained Ge - tannin complex with Ge content in the range of few percent can be further upgraded by roasting under atmospheric conditions into germanium oxide concentrate with Ge content over 20%.

It should be mentioned here, that in some cases, such as processing of primary raw materials enriched pyrometallurgically to Ge contents over 5%, the leaching may be also realized using

HCl – Cl2 gas system, whereby the crude GeCl4 can be separated, ready for purification either by multistage redistillation, or – by application of SX or IX methods.

The germanium–bearing leach solutions of sulphate or chloride nature can be processed alternatively by application of solvent extraction (SX) or synergistic solvent extraction (SSX) and ion exchange (IX) methods, using such organic solvent extraction reagents as: Kelex 100, LIX26, LIX63, Alamine 336, LIX26/KELEX, and – ion exchange resins from amberlite group, e.g. IRA400 [Safarzadeh, 2014].

The comprehensive review of SX and SSX systems used for Ge extraction from acidic sulphate solutions [Nusen, 2015]. provides the examples of Ge separation with Kelex100, LIX63, LIX26, DZEHPA + TBP, LIX63 + Ionquest 801, and others.

The Ge extraction from acidic chloride solutions can be effectively performed using Cyanex 301 and Cyomex 923 toluene solutions [Gupta, 2006].

All easily accessible information on germanium extraction using SX, SSX and IX methods concern the field of research works, while the described applications on industrial scale usually do not reveal neither reagent used nor particulars of extraction and stripping operations. It seems that Ge extraction with Kelex100 or LIX63 and stripping with NaOH solutions are probably applied in industrial practice in most cases where SX method for Ge recovery is applied (e.g. Teck Resources).

The published flowsheets of Ge recovery from primary sources are as a rule far from being precise, as could be seen in vague examples from the end of previous century [Scoyer, 2005]. The other germanium production processes descriptions may be found in the literature, e.g. [Liang, 2006], [Teck Resources, 2014], [Fayram, 2006], [Pu, 2013].

## 12.2.2.1    PRODUCTION OF GE CONCENTRATE FROM ZINC PLANT LEACH RESIDUE AT BLEIBERGER BERGWERKS UNION, AUSTRIA

Zinc concentrate, with 0.02% Ge, was treated in typical RLE process, with concentration of Ge in acid leach residue, which was thermally treated in modified Waelz furnace, with coke, giving Ge – Zn fumes (0.10 % Ge, 62% Zn). After leaching of these fumes, germanium was precipitated with tannic acid giving Ge – tannin concentrate (6 – 8% Ge, 40% Zn) intended for sale.
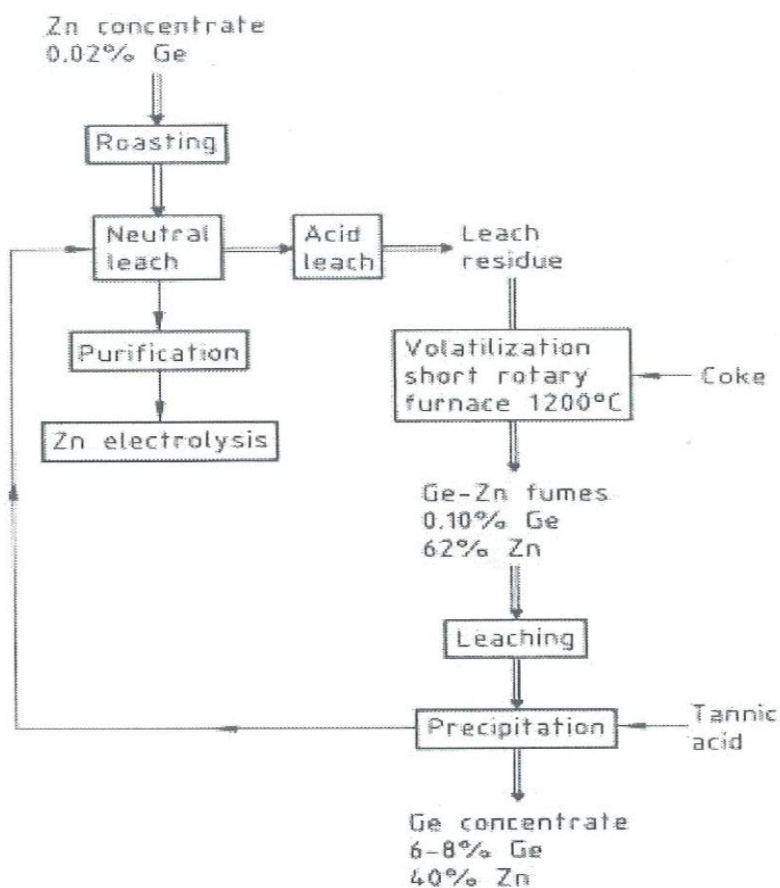
**Figure 1.** Production of a germanium concentrate: flow sheet of Bleiberger Bergwerks Union (BBU)
Location: Arnoldstein, Austria; Bleiberg mine. Estimated Ge capacity: 6 t/a.

## 12.2.2.2    PRODUCTION OF GE CONCENTRATE FROM ZINC PLANT LEACH RESIDUE AT JERSEY MINIERE ZINC AND METALLURGIE HOBOKEN – OVERPELT

The JMZ plant (TN, USA) processed zinc concentrates from Gordonsville and Elmwood mines, with 0.04% Ge. Germanium was concentrated in leach residue (0.5% Ge) and transferred for further treatment to MHO (Belgium), where this residue was leached. Germanium was next separated by SX method and stripped in alkaline solution, giving after hydrolysis rich Ge concentrate (50% Ge), regardless of the Ge concentration in the feed.
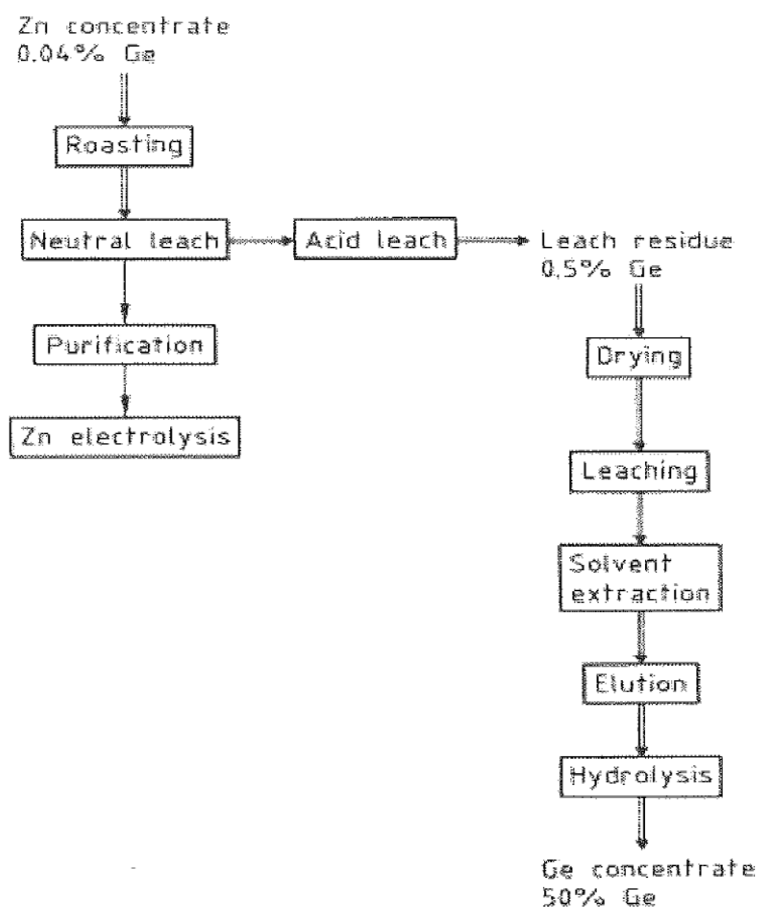
**Figure 2.** Production of a germanium concentrate: flow sheet of Jersey Minière Zinc (JMZ) and Metallurgie Hoboken-Overpelt (MHO)
Locations: JMZ at Clarksville, Tennessee, United States; Gordonsville mine. MHO at Olen, Belgium. Estimated Ge capacity: 65 t/a

### 12.2.2.3   PRODUCTION OF GE CONCENTRATE FROM CUGEGA ORE FROM APEX MINE  (UT, USA)

CuGeGa concentrate from Apex mine (0.065% Ge) was leached in $H_2SO_4$ solution with $SO_2$ gas for reduction of iron to divalent form. Leach solution was liberated from Cu through concentration with iron, and next germanium was precipitated with $H_2S$ gas to obtain Ge sulphidic concentrate (3% Ge). Gallium was then separated by solvent extraction, and – after stripping – precipitated by hydrolysis as Ga concentrate (8% Ga). The process described above was then improved toward metallic gallium product.
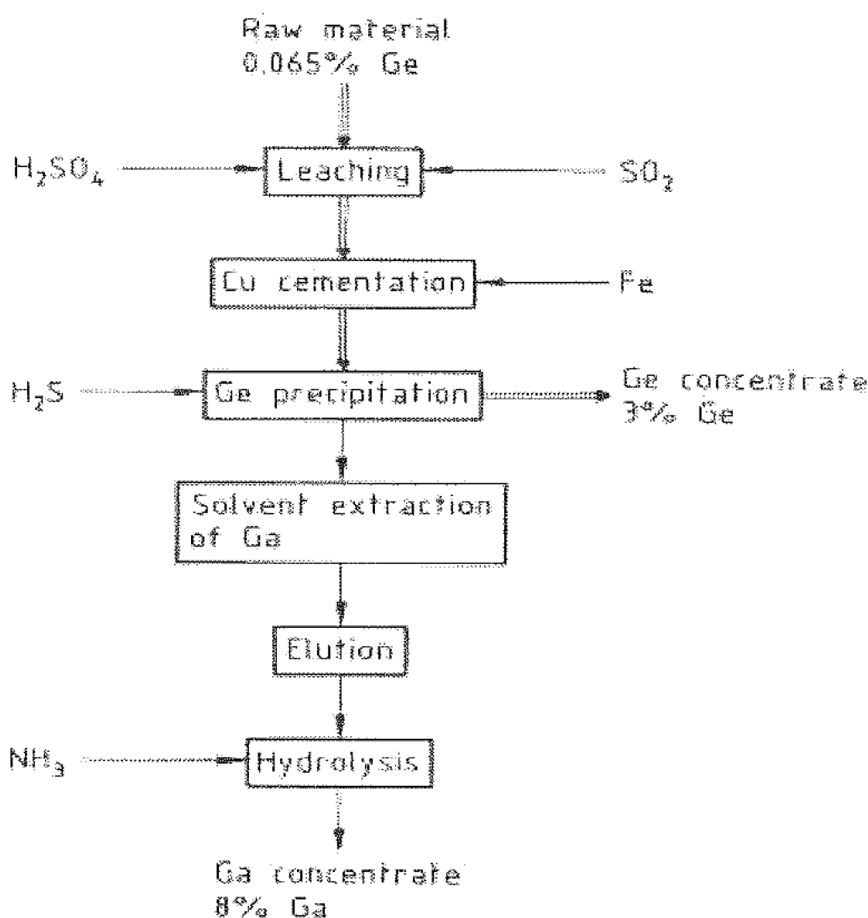
**Figure 3.** Production of a germanium concentrate: flow sheet of Musto Exploration.
Location: St. George, Utah, United States; Apex mine. Capacity: 18 t/a of Ge and 10 t/a of Ga.

### 12.2.2.4 PRODUCTION OF GE CONCENTRATE FROM ZINC CONCENTRATES AT ISP PLANT, PENARROYA (FRANCE)

Zn – Pb concentrate (0.015% Ge) and matte (0.01% Ge) from zinc plant at Pertusola (Italy), being a subsidiary of Penarroya, were processed together by Imperial Smelting Process. Ge was first concentrated in zinc phase (0.022% Ge), next purified in NJ distillation columns, where Ge was left in zinc still residue phase. After volatilization of zinc the germanium concentrate was produced and processed further for GeCl4, GeO2 and Ge metal.
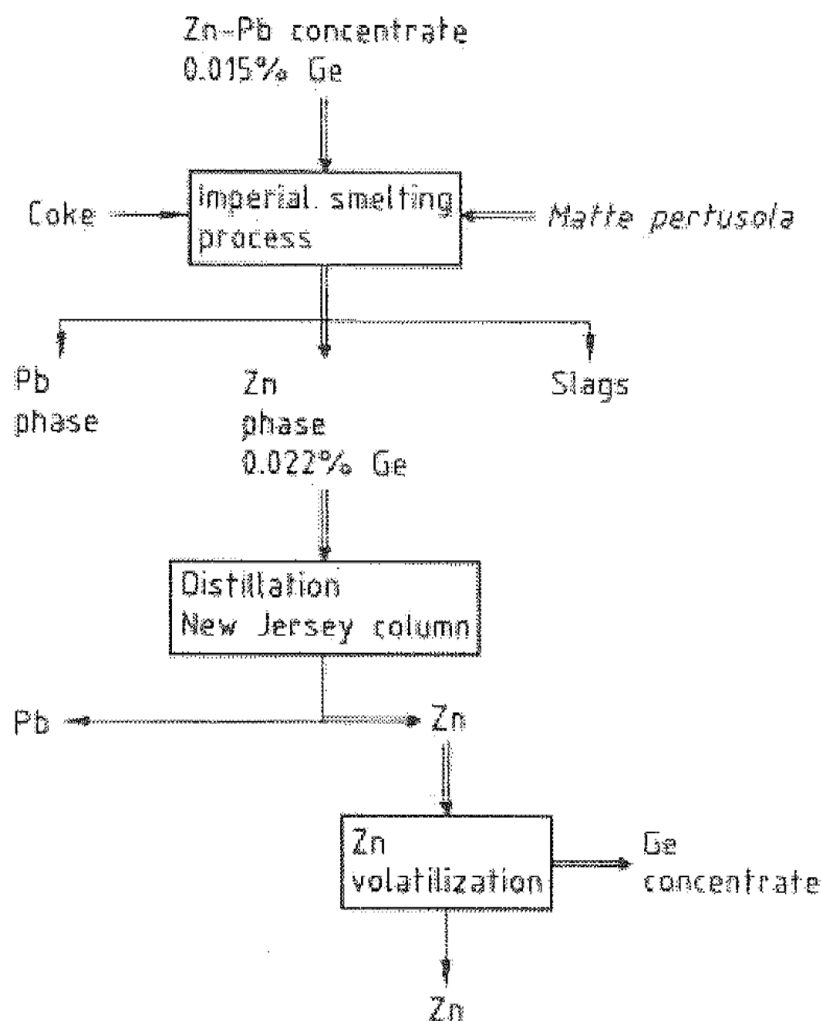
**Figure 4.** Production of a germanium concentrate: flow sheet of Peñarroya
Location: Noyelles-Godault, France; Saint-Salvy mine. Capacity: $GeO_2-GeCl_4$, 60 t/a; Ge metal, 30 t/a

### 12.2.2.5 PRODUCTION OF GE CONCENTRATE FROM ZINC CONCENTRATES AT ZINC PLANT PERTUSOLA (CROTONE, ITALY)

Zinc concentrates from Salofosa mine (0.02% Ge) were processed according to classic RLE technology, with concentration of Ge in leach residue (0.04% Ge). This residue was thermally treated (together with copper cement from zinc solution purification step) in reducing conditions (coke), giving matte (0.01% Ge), sent to be processed at Penarroya (fig. 4.) and PbZnGe fumes (0.1% Ge). These fumes were leached in site, and then germanium was precipitated, yielding Ge concentrate (7 – 35% Ge).
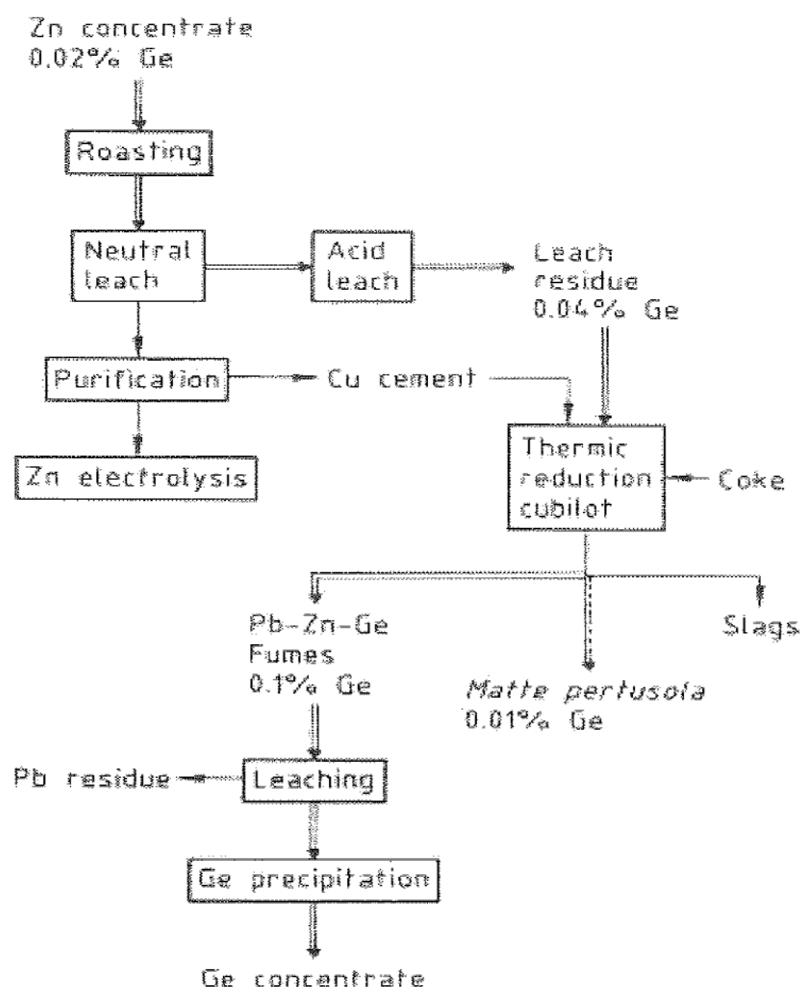
Figure 5. Production of a germanium concentrate: flow sheet of Pertusola
Location: Crotone, Italy; Salafosa mine.

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# 13 HAFNIUM

## 13.1 PRODUCTION LINES OF IDENTIFICATION FROM PRIMARY RESOURCES

Hafnium is a chemical element with symbol Hf and atomic number 72. Is a lustrous, silvery-gray tetravalent transition metal. Chemically resembles Zirconium and is found in many zirconium containing minerals and is thus difficult to separate. As zirconium, pure finely divided hafnium metal ignites in air.

### 13.1.1 OCURENCE

Haftium is estimated to be around 5.8 ppm of the Earth's crust by mass and it does not occur as a free element, but in solid solutions with zirconium: zircon (ZrSiO4), havy mineral sands ore deposits, pegmatites.

A major source of Zr and Hf is in Brazil and Malawi and in carbonatite deposits in the deposit of Mount Weld, Western Australia.

A potential source of Hf is trachyte tuffs contining Zr-Hf silicates eudialyte or armstrongite in Dubbo, New South Wales, Australia.

Hafnium is always being extracted or remains as a by-product from the extraction of Zr.

### 13.1.2 PRODUCTION

Only two significant actors are currently producing Hf: ATI Wah Chang (part of Alleheny Technologies Inc (NYSE:ATI) in Oregon, USA and CEZUS in Jarrie, France (Part of AREVA group PA:CEI). (ETF 2018).

### 13.1.3 USES

Hafnium is often used in filaments and electrodes as well as in semiconductors. Also, some superalloys contain hafnium in combination with niobium, titanium or tungsten.

Also, due to it's property of neutron absorber, hafnium is used in control rods in nuclear power plants. Also, it is important to be removed from zirconium alloys used in nuclear industry (GRE 2011).

## 13.2 REFERENCES

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# 14 HELIUM

## 14.1 PRODUCTION LINES OF IDENTIFICATION FROM PRIMARY RESOURCES

Helium is a chemical element with the symbor He and atomic number 2. It is a colorless, odourless, non-toxic, inert, monoatomc gas and is the first int eh nobel gas group. Helium the second most aboundant element after hydrogen in the universe and the most common is helium-4. It has the lowest boiling point among all the known elements. It was discovered by two Swedish chemists 1895, Per Teodora Cleve and Nils Abraham Langlet, which found helium emanating from the uranium ore clevenite.

On earth helium stands for 5.2ppm by volume in the atmosphere while the terrestrial helium is created by the natural radioactive decay of heavy radioactive elements from for example, thorium and uranium, as the alpha particles emitted by their decay consists on helium-4 nuclei.

This type of helium (radiogenic) is trapped with natural gas in concentrations as high as 7% by volume.

### 14.1.1 WORLD PRODUCTION AND RESERVES

The helium resources of the world, exclusive of the United States, were estimated to be around 31.3 billion cubic meters (USGS 2017).

In December 31, 2016, the total helium reserves of the United States were estimated to be 20.6 billion cubic meters. This included 4.25 billion cubic meters of measured reserves, 5.33 billion cubic meters of probable resources, 5.93 billion cubic meters of possible resources and 5.11 billion cubic meters of speculative resources.

The locations and the volumes of the major deposits, in billion cubic meters are: Quatar 10.1; Algeria 8.2; Russia 6.8; Canada 2.0; China 1.1.

A recent discovery of a very rich helium deposit has been done in Tanzania, where the helium is in up to 10% concetration and the company which stepped in of eventual production is called Helium One (HEL –O 2017).

Table 1. The helium world production and reserves as of January 2017

| Country | Production – All forms | | Reserves |
|---|---|---|---|
| | 2015 | 2016 | |
| United States (extracted from natural gas) | 66 | 63 | 3900 |
| United States (from Cliffside Field) | 22 | 22 | *included in the previous number |
| Algeria | 10 | 10 | 1800 |
| Australia | 4 | 4 | NA |
| Canada | <1 | <1 | NA |
| China | NA | NA | NA |
| Poland | 2 | 2 | 25 |
| Quatar | 49 | 50 | NA |
| Russia | 3 | 3 | 1700 |
| Other countries | NA | NA | NA |

| World Total (rounded) | 156 | 154 | NA |

## 14.1.2 PRODUCTION

In Algeria, the helium is produced by Helison Production Spa, a joint venture between the Algerian gas and oil company Sonatrach and The Linde Group, which has started operation in 2006 in Skikda, (East of Algeria). The plant has been designed and build by Linde Engineering. (Gasworld.com, from 29th of November 2007).

The nominal capacity of the Skikda plant is 600 mmscft/year of liquid helium (16 million Nm3/year), according to the company webpage (HEL 2017).



Fig x. Image of part of the production plant, retrieved from (HEL2017).

Sonatrach supplies the feed gas which is a mixture of helium, nitrogen and methane to Helison from their three LNG plants they own and operate in Skikda.

According to the source, during the helium production process, the nitrogen is separated, liquefied and delivered back to Sonatach for use in the industry while the methane is returned to LNG complex and used to produce steam. This way the Helison plant is emission-free.

## 14.1.3 USES

It's unique combination of properties makes helium very sought-after commodity for a lot of applications.

Just to name a few applications: MRI, laboratory, controlled atmospheres, breathing, fibre optics, leak detection, welding, purging/pressurizing, other cryogenics, lifting/ballons, electronics, etc.

## 14.2 REFERENCES

(HEL-O 2017) http://www.helium-one.com/about-us/strategy-mission-statement/ (retrieved December 2017)

## 15  INDIUM

### 15.1 PRODUCTION LINES OF IDENTIFICATION FROM PRIMARY RESOURCES

The main application of indium is observed in production of indium-tin oxide, which is used in LCD displays. Indium-based semiconductors may be found in light emitting diodes (LED), solar cells, photodiodes and photodetectors. It is also used as a component of solders and other low-fusible alloys, dental alloys and surface coatings. Indium is mainly produced by processing of residues and dusts from zinc smelting. Minor amounts of indium are also obtained during smelting of copper- and tin-based ores.

### 15.2 PROCESSING TECHNIQUES RECOGNITION AND ANALYSIS

#### 15.2.1 MINERAL PROCESSIN

There are only few known indium minerals - e.g. roqesite (CuInS2) and indite (FeIn2S4). None of them is present in sufficiently high concentrations to allow economical extraction process. However, indium is present as a trace element in the ores of other more abundant metals (zinc, copper and tin) in such minerals as chalcopyrite, cassiterite, stannite and sphalerite.

#### 15.2.2 METALLURGICAL EXTRACTION

Most of indium (ca. 95%) is produced as a by-product of zinc extraction. Its other sources are copper and tin residues. Technologies used for recovery of indium require high capital cost. Formerly, when indium demand was low it was supplied from processing of large amounts of low-quality zinc ores. At the end of the 20th century improvement in post-production slime processing made indium recovery process more beneficial.

The biggest world producer of indium is China, accounting for almost half of world production [**USGS 2015**]. The other significant indium suppliers are South Korea, Canada and Japan.

Information about production techniques of indium are not widely available. There are few general concepts described, e.g. in manufacturers report. However, most of information concerning indium recovery technologies is proprietary.

##### 15.2.2.1     PRODUCTION FROM ZINC ORES

The most of zinc (ca. 90%) is produced by hydrometallurgical processes. Typical hydrometallurgical smelting process is composed of four steps: Waelz process, leaching, purification and electrowinning. Low grade zinc concentrates are enriched using flotation to achieve 80-90% content of sphalerite. Then, concentrates are roasted. Obtained zinc calcine is leached and zinc is transferred to a solution.

General technology for indium recovery is described by Ullmann's encyclopaedia [**Noel, 2002**]. Zinc oxide is leached using diluted sulphuric acid. Zinc is partially removed with the solution and the residue containing indium is leached again with diluted hydrochloric acid. During this step most of lead is removed in the residue along with smaller amounts of indium and arsenic. The filtrate from previous step is neutralised using soda and most of the indium is precipitated. The precipitate is then leached using sodium hydroxide solution to remove impurities like

arsenic and remaining zinc. After this step indium hydroxide precipitate is leached in diluted hydrochloric acid. Purification of indium is done by cementation of copper and arsenic with iron and cementation of tin and lead with indium powder. Finally, metallic indium is obtained by cementation with aluminium. The diagram of this process is shown in Figure 1.
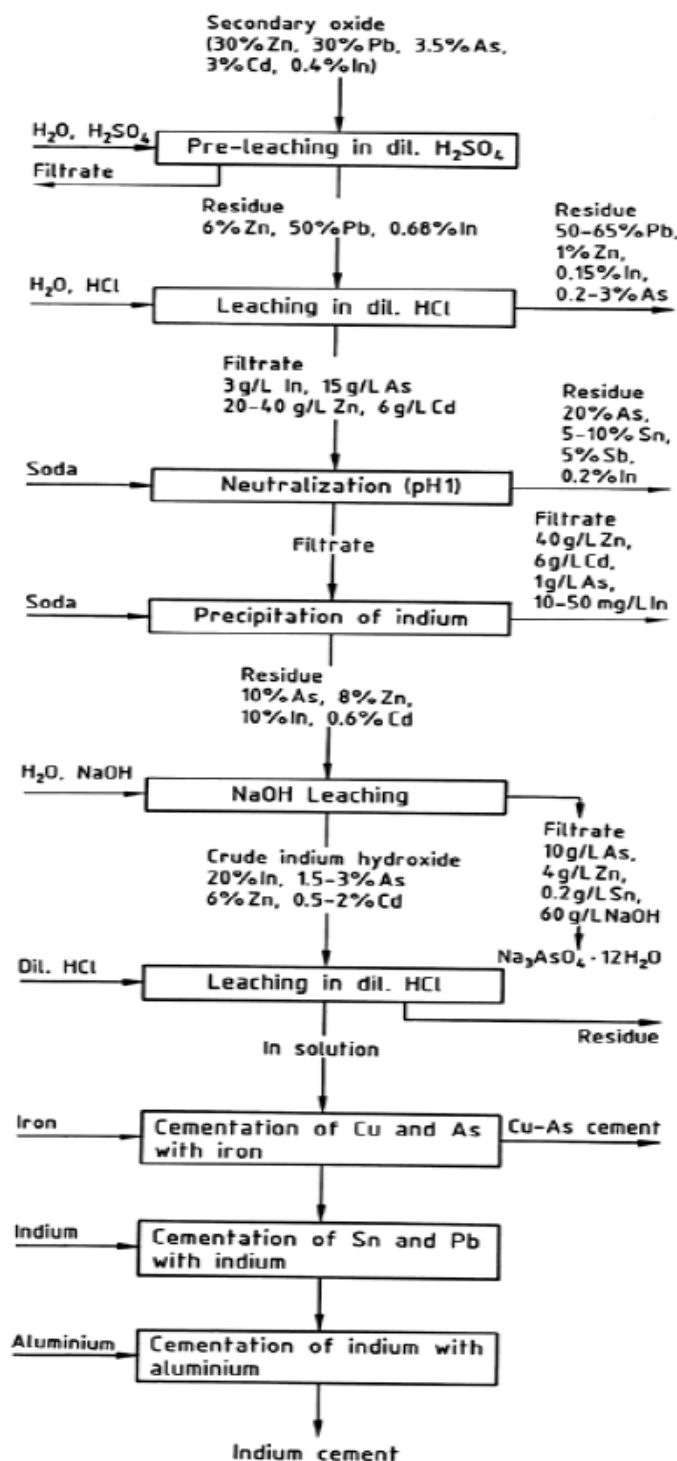


**Figure 1.** Indium recovery from secondary zinc oxides.

Slightly different method for indium recovery is described by [**Schwartz-Schampera, 2014**]. In the first purification step cadmium is removed from the solution and purified solution is then electrolysed and metallic zinc is deposited on aluminium plates. Zinc solution is refined in jarosite process, during which iron and up to 60% of indium and germanium is removed from the solution. The remaining solution may contain up to 600 ppm of indium. During electrolysis indium precipitates to form anode slime. Depending on the ore the slime may be used as indium source. Indium may be recovered from anode slime and other process intermediates using hydrochloric or sulphuric acid. Another way is to process the slimes in lead furnaces. During imperial smelting process (ISP) about half of the indium is enriched with lead. The rest may be found in blast-furnace slag and may be recovered by roasting in rotary furnace and slag fuming. Separation of indium from tin is performed within slagging and electrothermal processes. Within electrolytic operations indium anode and slime of 20-25% In content is obtained. Crude indium metal (ca. 99% In) is obtained by chemical processing of the slimes, e.g. by application of solvent-liquid extraction followed by electrorefining [**Schwartz-Schampera, 2014**].

One of the examples of indium recovery from zinc concentrates was presented by Kidd Creek smelter in Timmins (Canada). The smelter processed material containing ca. 270 ppm indium. Indium processing started with sulphidic zinc concentrate smelting. Obtained zinc calcine was leached. The indium containing residue was then subjected to two-step dissolution process. Firstly, iron was selectively removed in the form of jarosite. Secondly, metal-rich Cotrell ash from copper refinery was added to the solution. Copper containing residues as well as lead-silver were separated and indium containing solution was subjected to solvent extraction. Pure indium was obtained after a series of precipitation-dissolution processes [**Jorgerson and George, 2004**]. The diagram of the process is shown in Figure 2.

Teck Cominco Ltd. located in Trail, British Columbia, Canada, recovers indium from gaseous streams [**Fthenakis, 2007**]. Fumes from lead smelter with 0.05-0.2% indium are transferred to zinc facilities, where are leached to remove lead residue. Slurry is settled to remove lead residue and solution is subjected to second leaching step. After partial neutralisation by direct fumes addition and ferric ion, precipitate which contains germanium, indium, arsenic and antimony is obtained. The precipitate is then directed to indium recovery plant.

Umicore uses "Harris Process" [**Schwartz-Schampera, 2014**] to recover indium during lead refining. The composition of slag is changed by selective oxidation using hydroxides and nitrides of alkali metals. Impurities are removed with lead.

La Oroya smelter in Peru [**Alfantzi and Moskalyk, 2003**] produced indium from concentrates obtained from Centromin SA. Indium was recovered as a chloride ($InCl_3$) using coke reduction of lead bullion followed by addition of lead and zinc chlorides. Then tin and lead were removed from the solution and after zinc powder addition pure indium was obtained in the form of a sponge.

Generally, recovered indium has a >99% purity. Lower-grade metal is then refined to 4N (99.99%) and higher purity using zone smelting and electrolytic refining.
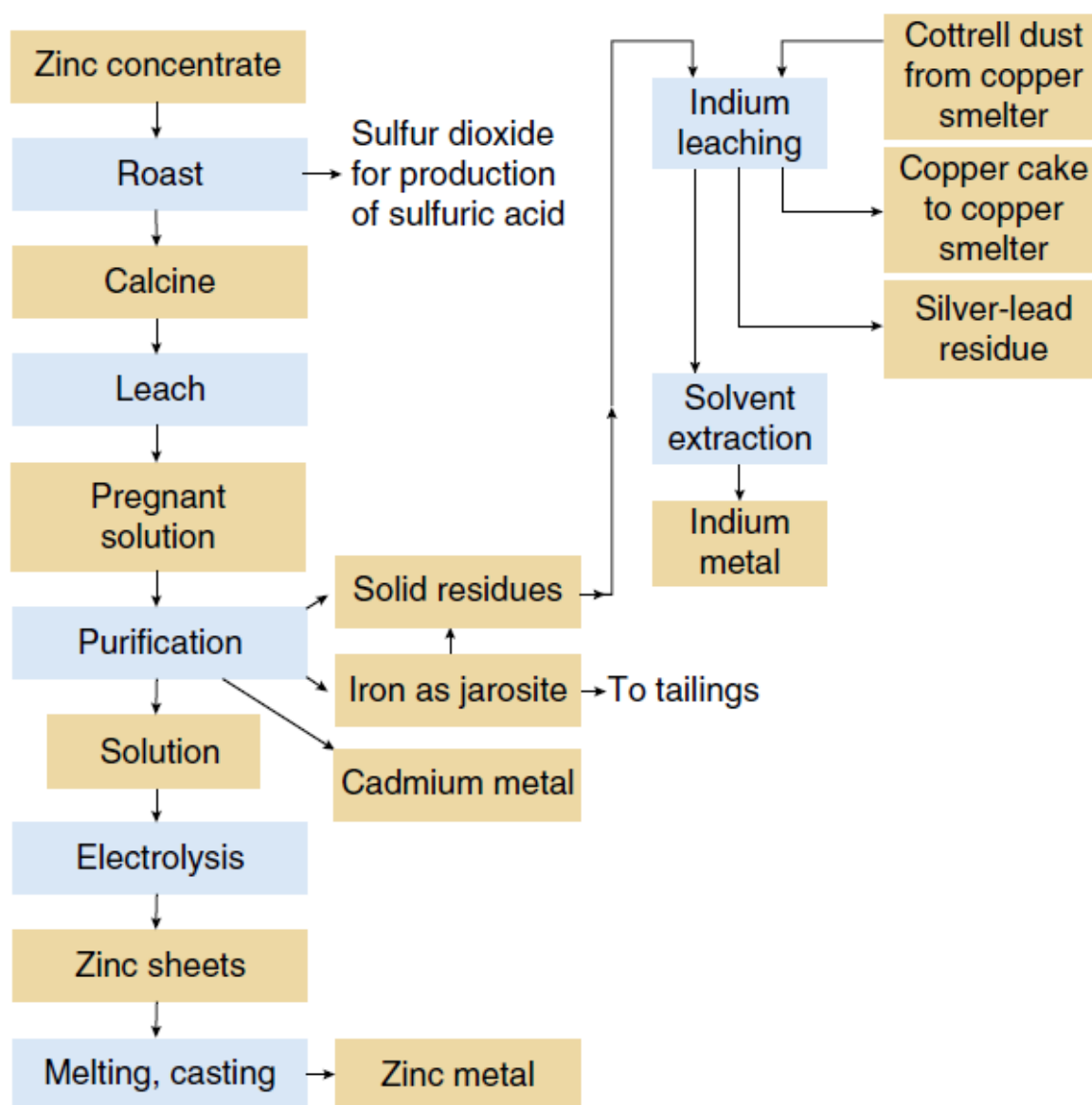
**Figure 2** Block diagram of indium recovery based on Kidd Creek smelter [**Schwartz-Schampera, 2014**]

## 15.2.2.2    PRODUCTION FROM COPPER ORES

Despite relatively high concentrations of indium in copper ores recovery of indium from copper concentrates is not widely applied. The main reason is very small grain size of the ores making recovery process unprofitable. However, there are reports that Urals Mining and Metals Co (UMMC) [**USGS, 2010**] launched indium recovery from copper production residues in 2006. The production output was estimated at 5 tonnes per annum. No more information about the process is available.

## 15.2.2.3    PRODUCTION FROM TIN ORES

Indium may be found in Bolivian tin ores [**Anderson, 2012**]. However, it is not recovered at place, but concentrates are processed mainly in Eastern Asia – China and Japan.

Indium was formerly recovered in Capper Pass in Great Britain [**Alfantzi and Moskalyk, 2003**]. One of the part of tin recovery process was electrorefined tin chlorination. The produced tin chloride slag contained less than 3% of indium. Then most of tin was precipitated during neutralisation. After that indium sponge was obtained by zinc cementation. The product of 95% purity was electorefined to get 99.5% purity indium cathode, which then was recasted to 99.97% anode in the second-step electrolysis.

The Novosibirsk Tin Plant (NOKN) [**Schwartz-Schampera, 2014**] applies vacuum refining for production of lead-tin alloys with elevated indium concentrations (up to 2000 ppm). The alloy is melted in 20-tonne vessel and then indium is selectively recovered. Other residues which contain at least 1000 ppm indium may be also processed using this method.

## 15.3 PROCESSING OF MINE TAILINGS AND RESIDUES

Formerly, when indium demand was at significantly lower levels than nowadays the slags and other residues which contain indium were not processed. Development of extraction techniques and increasing indium prices may make it beneficial to recover indium from mine tailings, slags and other indium-bearing post-production wastes.

One of the examples of residues which are considered as indium sources is Zeehan in Tasmania (Australia) [**Werner, 2017**]. The smelter was operating there between 1889-1913 by The Tasmanian Smelting Company. After the 2nd World War the site was abandoned causing significant impact on environment. The slag deposits are now owned by Intec Environmental. Pilot scale recovery processes were already done.

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# 16  MAGNESIUM

## 16.1 PRODUCTION LINES OF IDENTIFICATION FROM PRIMARY RESOURCES

### 16.1.1 GLOBAL PRODUCTION

The world's magnesium primary production is dominated by China. No primary production of magnesium is taken place in Europe. According to United States Geological Survey in 2015, one million ton magnesium was produced in the world, dominantly by China and with some production in Russia, Brazil and Israel, as shown in Figure 1. Other countries with some primary production of magnesium is US, Turkey, Ukraine, Kazakhstan and Republic of Korea, all together about 50 000 tons of magnesium.
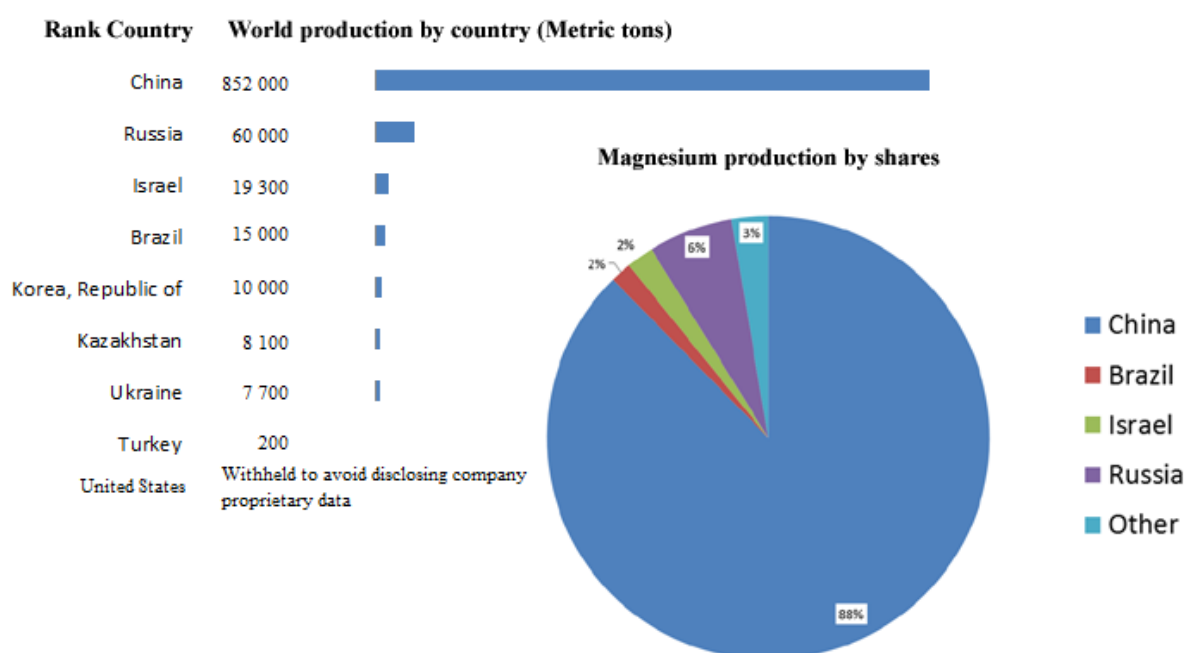


Fig. 1 Global magnesium primary production by amounts and by shares in different countries in 2015 (in total around one million tons). [1,2]

The world production capacity is significant larger than the production, c.f. figure 2. The global production capacity is roughly 1.9 million tons. [2] The largest part of the Chinese production is located in the province of Shanxi.
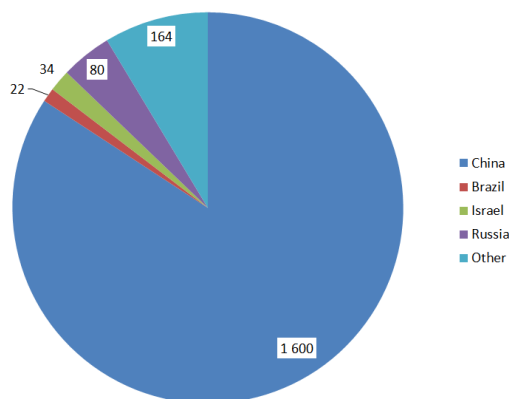
Fig. 2 Estimated global magnesium primary production capacity in 2015 (in 1000 tons) [2]

## 16.1.2 APPLICATIONS

End key market sectors for magnesium are die-casting, aluminium alloying, iron and steel sector and Other Uses. Die-casting can further be divided into automotive or non-automotive applications. The world market for magnesium in 2008 is shown in Figure 3.



**2008, Total 626 kton**
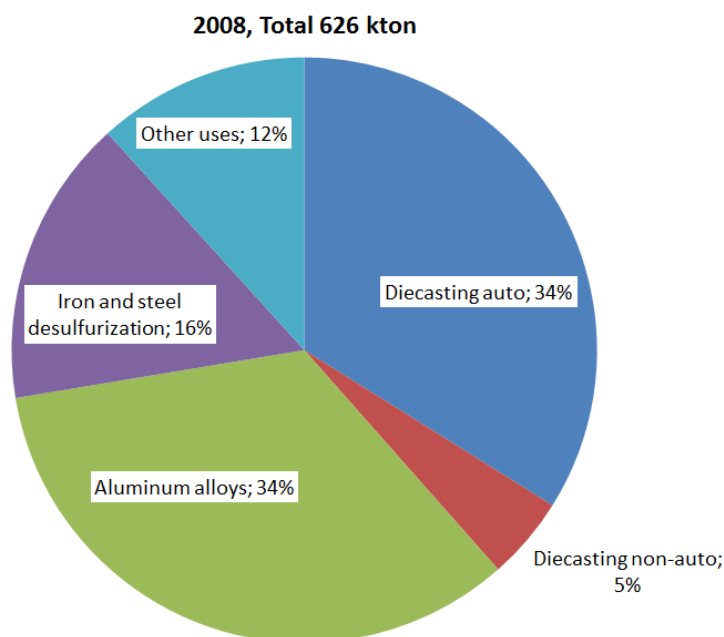
Fig. 3 World market for magnesium [2]

Magnesium used in die-casting is normally alloyed with aluminum, manganese, silicon and other minor metals. Magnesium for die-casting in automotive industry can be structural applications and non-structural applications, separated into crashworthiness requirements. Examples of non-structural applications are transmission cases, transfer cases, valve/cam covers, clutch housings, electric motor/alternator housings, intake manifolds and oil pans. Examples of structural applications are steering wheels, instrument panels/cross car beams, seating

systems, brake and clutch brackets, steering column parts and airbag housings. Magnesium alloys in structural applications benefits from its high ductility and impact strength properties. [1] The main driver for using magnesium in vehicles is reducing the vehicle weight that strengthens fuel economy. The strength to density ratio of magnesium alloys, especially structural application, is higher than for both aluminum alloys and steel.

The non-automotive die casting markets can be referred to as the 3C market (computers, communications and consumer). Examples of applications where the light weight of magnesium alloys are desired are laptop computers, camera housings and mobile phones.

The largest single use of magnesium is as an alloy with aluminum. Typically 1 to 6 % of magnesium is needed to increase strength, stiffness, weldability and corrosion resistance of aluminum alloys. Packaging accounts for 50% of the magnesium demand in aluminum alloys. Examples are beverage cans, where approximately 1.1% magnesium is used in the can body and 4.5% in the lid. Transport industry accounts for 35% of the magnesium demand in aluminum alloys, e.g. in marine applications due to the increased corrosion resistance. [1]

Magnesium is widely used in the iron and steel sector. Fine grained magnesium is used as a desulphurization agent of hot metal (i.e. liquid iron from blast furnace process), in the pre-treatment prior to BOF steelmaking. The magnesium is normally blended with fine grained caustic lime and the blend is injected into the hot metal where the magnesium reacts with sulphur to form magnesium sulphides.
Magnesium is also used in the production of nodular iron in order to cause the graphite in iron to nucleate as spherical particles and thereby impart both strength and ductility of iron castings.

Other uses of magnesium include chemical applications, metal reduction, gravity casting and wrought products and pyrotechnics. Examples of chemical uses are to prevent galvanic corrosion where magnesium is used as anodes to suppress corrosion. Magnesium metal is chemically active as a powder in pyrotechnical applications. One historical important application of magnesium powder was in military flares and tracer bullets during World War I.
Magnesium is an efficient reductant in the production of e.g. metallic titanium, beryllium, zirconium, calcium and hafnium.
The production of gravity casted magnesium and wrought magnesium alloys are small compared with die-casting. Most wrought alloys are used in specialist niche applications such as printing industry and military applications. Wrought magnesium alloys have after forming a higher tensile strength compared with the compressive strength.

## 16.2 PROCESSING TECHNIQUES RECOGNITION AND ANALYSIS

Magnesium was discovered about the same time as aluminum. Sir Humphrey Davy first isolated aluminum in 1807 and identified magnesium in 1808. The source of magnesium can be from sea water, brine, dolomite, magnesite or carnallite. In the electrolytic routes the magnesium metal is won from magnesium chloride and in the thermal routes the magnesium production involves a ferrosilicon reductant.

### 16.2.1 ELECTROLYSIS PROCESS FOR MAGNESIUM PRODUCTION

There are two main anhydrous routes for producing dehydrated magnesium chloride cell feed, c.f. Fig 4. The first main route involves chlorination of magnesium oxide (MgO) or magnesite ($MgCO_3$) in presence of carbon or carbon monoxide.

The other main route is dehydration of aqueous magnesium chloride solutions (brines) or hydrous carnallite.
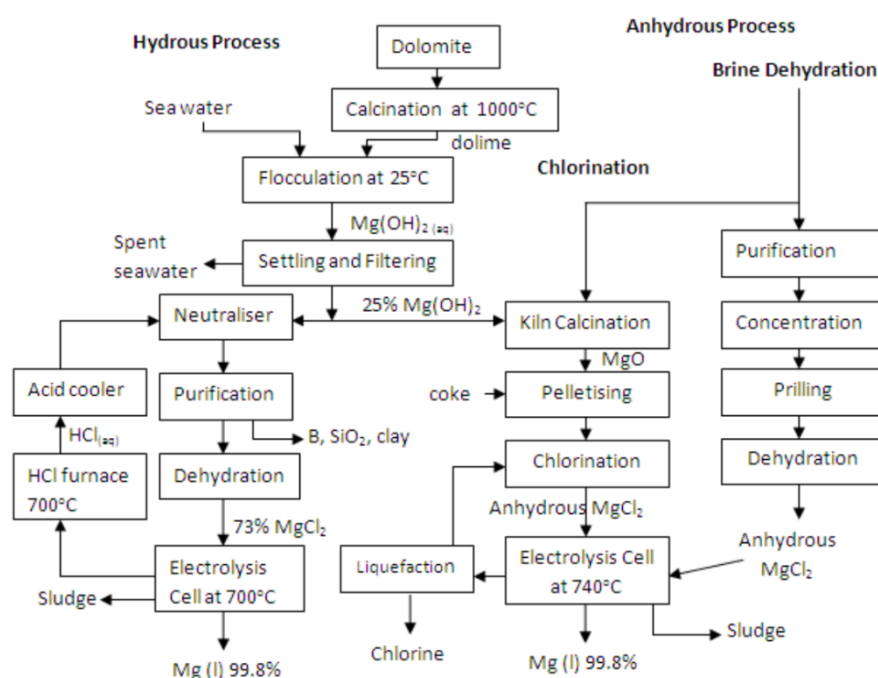


Fig. 4 Flowsheet of electrolytic routes for magnesium production [3]

In the former magnesium process of Norsk Hydro at Becancour plant (Canada) the production followed five steps, showed in fig 5. First magnesite rock was dissolved with concentrated hydrochloric acid, forming magnesium chloride. Most impurities are removed be precipitation. Next step is dehydration by evaporation and then the almost supersaturated solution is centrifuged to produce a micro-pelletised product (prill). The chemical water is then removed with hot air and hydrochloric acid gas. The third step is the electrolysis, where the anhydrous magnesium chloride prills are fed into an electrolyte ($NaCl_2$-$CaCl_2$). The electrolytic decomposition of magnesium chloride releases large amounts of chlorine gas. This gas is in the next step burnt together with hydrogen and absorbed into water to form concentrated hydrochloric acid to be recycled to previous steps. In the last step the liquid magnesium metal is brought to the foundry, where pure magnesium or alloyed magnesium is produced and casted into ingots or bars.
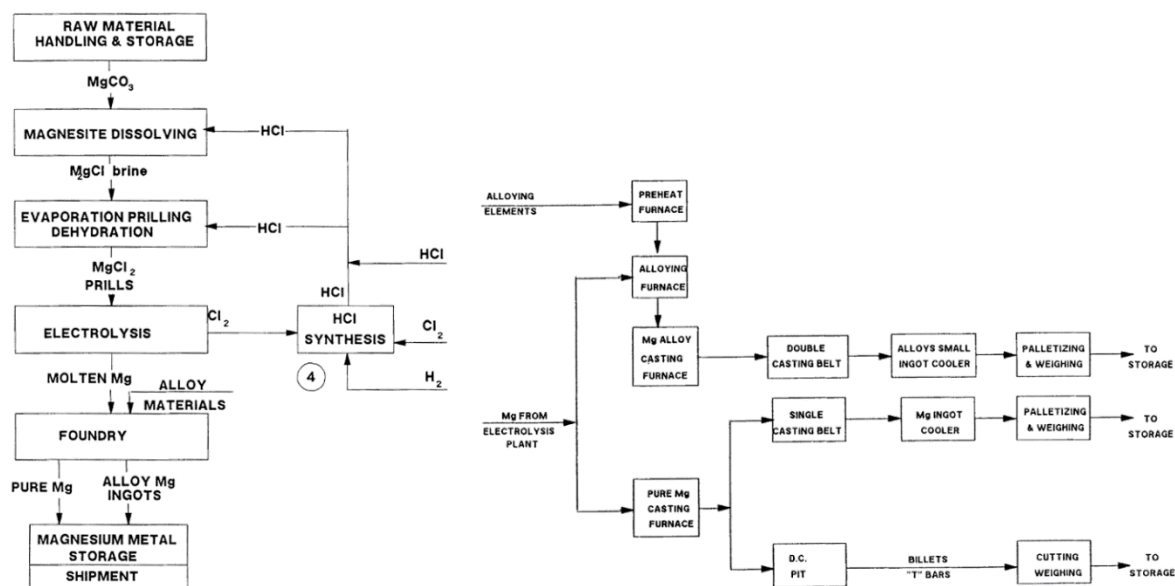
Fig. 5 Becancour magnesium plant, to the left a flowsheet overview and to the right the foundry[4]

Brines containing of ~34% magnesium chloride can be derived as a by-product from the potassium industry or produced by dissolving magnesium containing minerals in hydrochloric acid. Naturally occurring dilute brines are concentrated by solar evaporation. In the Dow Chemical process [5] hydrous magnesium chloride is fed as a cell feed. Magnesium hydroxide precipitated from seawater with calcined dolomite is dewatered on rotary filters. Sulphuric acid is added to precipitate excess calcium and removed by filtration. The brine is further concentrated to 35% magnesium chloride with waste heat.
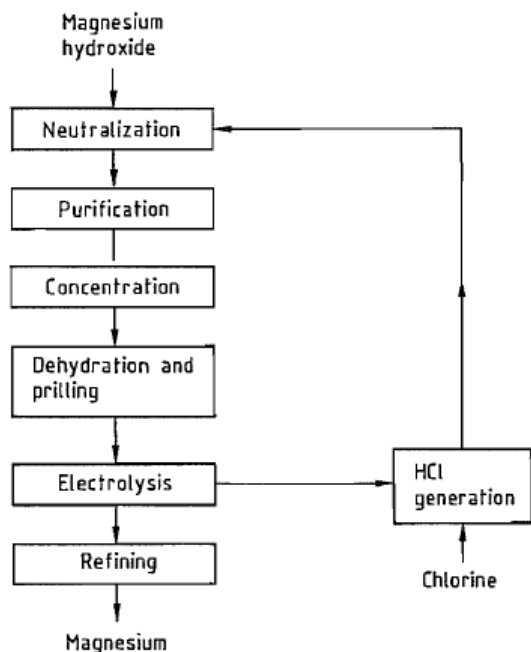


Fig. 6 Flow sheet for magnesium production via dehydration of seawater (Dow Chemical) [5]

The magnesium is electrolyzed in a molten mixture of alkali chlorides (electrolyte) at 700-800°C. The magnesium is lighter than the chlorides and rises to the surface. The different concepts have slightly different cell designs.

## 16.2.2 THERMAL PROCESSES FOR MAGNESIUM PRODUCTION

All industrial thermal processes for magnesium production are based on reduction of magnesium oxide with ferrosilicon. Magnesium oxide is provided mainly from calcined dolomite (MgO CaO). The base reaction is $2CaO_{(s)}$ + $2MgO_{(s)}$ + $(Fe)Si_{(s)}$ → $2Mg_{(g)}$ + $CaSiO_{4(s)}$. There are three different principles for the reaction chamber:

- Externally heated retorts in the Pidgeon process
- Internally electrical heated reactors in the Bolzano process
- Internally electrical heated reactors with molten slag in the Magnetherm process

The most dominant magnesium production process is the Pidgeon process. The first attempts trying to find a way reducing magnesium by a thermal process directly from dolomite were made before WWII in Germany. The process consisted of a resistor furnace with an electrical heating up to 1400°C under vacuum. Dr. L. M. Pidgeon of the Canadian Research Council developed the thermal process that became known as the Pidgeon Process. This process used calcined dolomite and ferrosilicon ground, blended and briquetted into pellets that were charged into closed end, externally heated retorts. A 5,000-tpy plant was built at Haley, Ontario and quickly ramped up in production. This plant is still in operation today.

During the 90th the Chinese magnesium production, mainly based on the Pidgeon process, rapidly increased. The production increased at an annual rate of >40%. Low cost labor, available raw materials and high magnesium prices were strong contributors to this development. The starting material for the Pidgeon process is dolomite, calcium magnesium carbonate, which is calcined and then crushed together with ferrosilicon and the blend is formed into briquettes. These briquettes are fed into retorts in a furnace, which is indirectly heated to 1100-1200°C often using coal. The magnesium is reduced with ferrosilicon to form metal vapor. The vapor is sucked from the retort by applying vacuum and immediately condensed by applying indirect water cooling outside the retort, c.f. fig.7. After 10-12 hours of reduction, the condensed magnesium is collected. The remaining material, mainly a di-calcium silicate slag, is emptied manually and then the retort can be filled with new briquettes. The slag can be utilized in cement manufacturing. The condensed magnesium, magnesium crowns, is re-melted and casted into ingots. A schematic flow scheme is showed in fig.8.
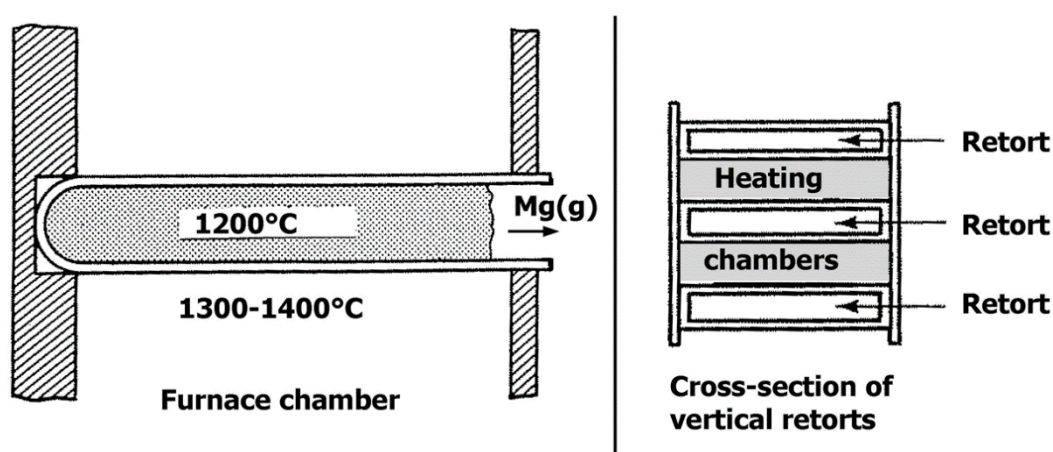


Fig 7. Principal of Pidgeon process
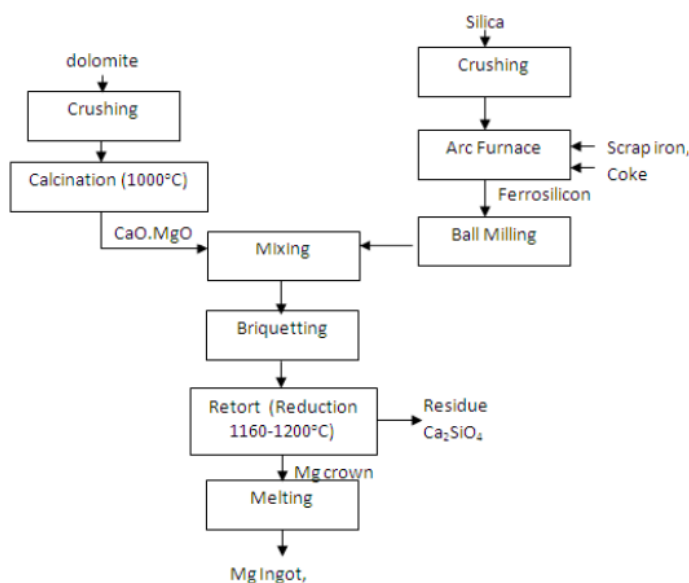
Fig 8. Schematic Flowsheet of the Pidgeon process [3]

The Bolzano process, developed in Italy and is now in operation in Brazil under the name of Brasmag, is shown in fig 9. Briquetted blend of calcined dolomite and ferrosilicon is charge inside the furnace that is internally electrically heated. The process operates at 1200°C and <400 Pa. Magnesium vapor condenses inside the water-cooled condenser into magnesium crowns. The process cycle is 20-24 hours.



a Steel mantel; b Refractory; c Removable charge pack; d Charge briquettes; e Charge support; f Electric heating connection; g Removable condensor; h Condesed magnesium
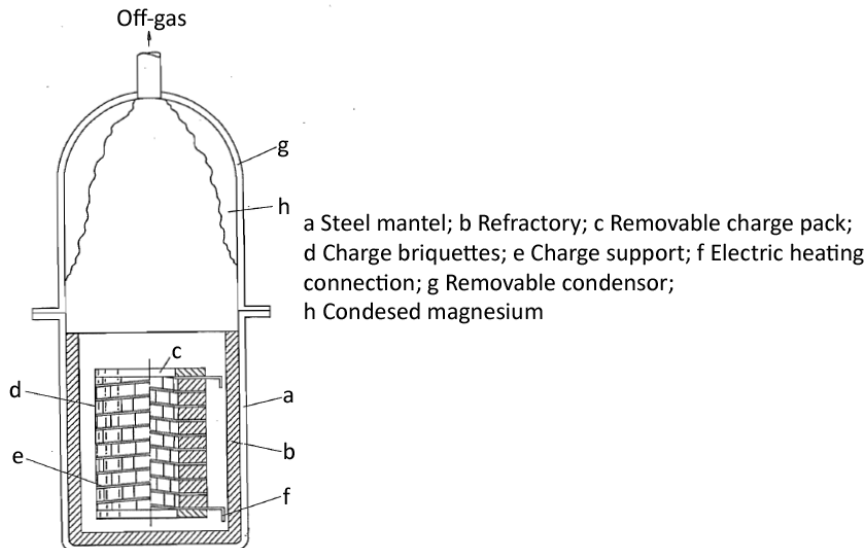
Fig. 9 Bolzano process [5]

The Magnetherm process, developed by Pechiney Électrométallurgie in France during the 1950s, is also based on ferrosilicon reduction, but instead of forming a solid dicalcium silicate slag as in the Pidgeon and Bolzano processes the Magnetherm process operates with a partly molten slag. The Magnetherm process operates at 1550-1600 °C under vacuum, showed in fig. 10. Calcined dolomite, alumina/bauxite and ferrosilicon are fed to the slag through the lid of the reactor under vacuum. Electrical power input is conveyed through a water cooled copper electrode from the top to the bottom graphite lining.  The formed magnesium metal vapor

condenses in a separate condenser system. The process cycle takes 18-24 hours and ends with the slag tapping. The slag can be used in the cement industry.
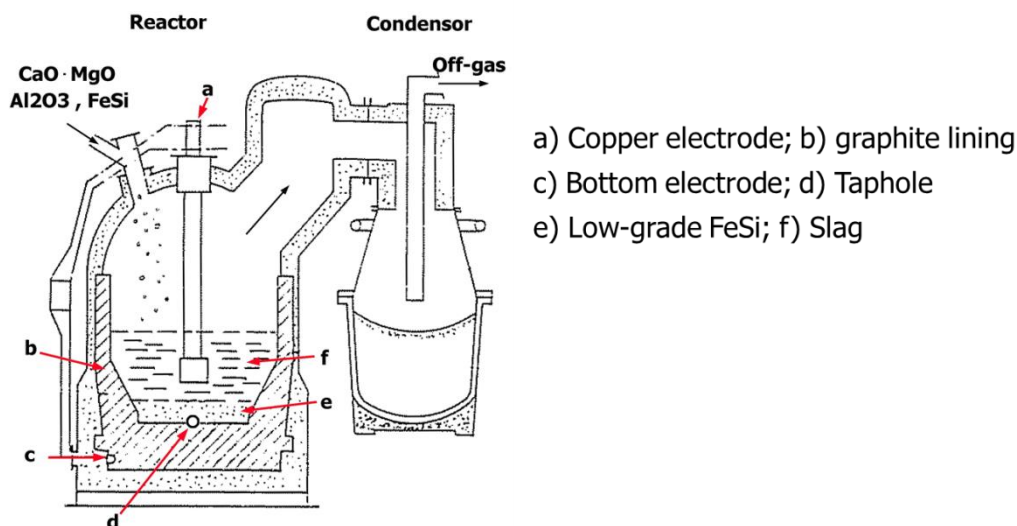


Fig. 10 Magnetherm process [5]

All magnesium processes are followed by refining to remove impurities, alloying (if magnesium alloys are to be produced) and casting into ingots, billets, slabs or granules. The iron content of the metal can be reduced by adding e.g. manganese. Nonmetallic inclusions e.g. chlorides have a higher density than the magnesium metal and will sink to the bottom of the melt.

## 16.3 PRIMARY VALUE CHAIN, IDENTIFICATION OF SECONDARY RESOURCES AND LOSS OF MAGNESIUM INTO THE ENVIRONMENT

Magnesium does not occur in elemental form in nature, although it is the eight most abundant element in the earth's crust. There are two primary value chains of magnesium (magnesium mineral or seawater ⮕ magnesium chloride ⮕ magnesium metal and magnesium mineral ⮕ reduction with ferrosilicon ⮕ magnesium metal respectively). Examples of secondary resources are return material from different stages of casting and metal working in the foundry and EOL magnesium products.

Possible secondary resources for magnesium production from EOL products magnesium alloys for die-casting and wrought products. Magnesium used in aluminium alloying will also be recycled.

Examples of loss of magnesium to the environment are when the magnesium is used in the iron and steel sector, i.e. for de-sulphurisation of hot metal and production of nodular iron. Also magnesium used in chemical applications and pyrotechnical applications is not possible to recycle.

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# 17  NATURAL GRAPHITE

## 17.1 PRODUCTION LINES OF IDENTIFICATION FROM PRIMARY RESOURCES

### 17.1.1 GLOBAL PRODUCTION

Graphite can be classified as natural graphite and synthetic graphite. Natural Graphite is a mineral consisting of graphitic carbon. According to the crystallinity, natural graphite is subdivided into three types, namely, amorphous graphite, flake graphite and crystalline graphite. [1], [2] The properties of different types of natural graphite are summarized in **Table 4** and a description of them is shown as follows.

- Amorphous graphite. Amorphous graphite is found as minute particles in beds of mesomorphic rocks, such as coal, slate or shale deposits. The graphite content in the mine ranges from 25% (or 15%) to 85% dependent on the geological conditions. Amorphous graphite is the most abundant.
- Flake Graphite. Flake graphite is found in metamorphic rocks uniformly distributed through the body of the ore or in concentrated lens shaped pockets with carbon content varying between 5-40%. Flake graphite is less common in the world.
- Crystalline Graphite. Crystalline graphite is believed to originate from crude oil deposits. Vein graphite fissures are typically between 1 cm and 1 m in thickness, and are typically > 90% pure.  Crystalline graphite is rather rare and it accounts for only 1% of the world production. At the moment it is only commercially mined in Sri Lanka.

In 2016 the global mine production of natural graphite amounts to 1.2 million tons and the production is dominated by China (61%), India (14%) and Brazil (7%), as shown in **Figure 12**.[3] The world top 12 producers of natural graphite are listed in **Table 5**.
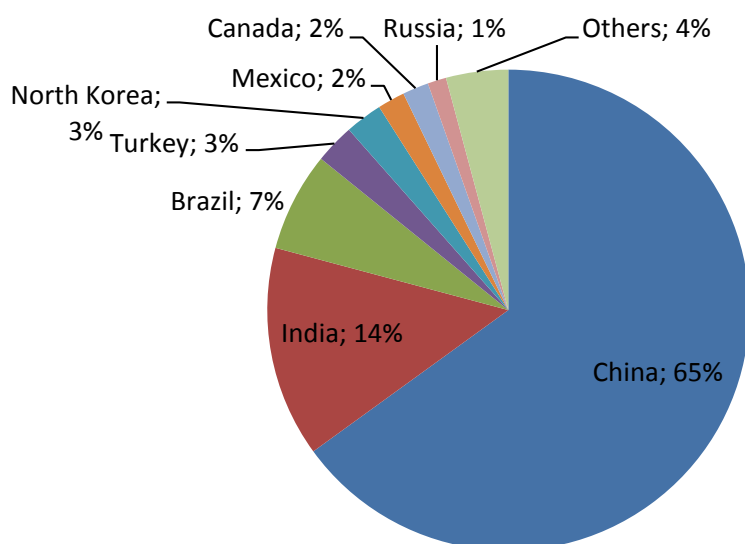


**Figure 12** Global mine production of natural graphite (1.2 million tons in total in 2016).[3]

**Table 4** Properties of different types of natural graphite and their different applications.

| Type | Quality | Occurrence | Applications | Prices | Deposits |
|---|---|---|---|---|---|
| Amorphous | 70-85% C<br><br>Most abundant | Refers to its very small crystal size and not to a lack of crystal structure | Used for lower value graphite products<br>Brake linings, refractories, steelmaking | Lowest priced graphite | Large amorphous graphite deposits in China, Europe, Mexico, and the USA |
| Flake / crystalline flake | 85-90% C<br><br>Less common | Occurs as separate flakes that crystallised in metamorphic rock | Can be processed into expandable graphite for many uses, such as flame retardants<br>Batteries, brake linings, lubricants, refractories | Can be four times the price of amorphous | Austria, Brazil, Canada, China, Germany, and Madagascar |
| Vein / lump | 90-96%<br><br>Rarest | Occurs in veins along intrusive contacts in solid lumps | Steelmaking | The most valuable | Only commercially mined in Sri Lanka |

**Table 5** World top 12 Producer of natural graphite.[4]

| | Company | Location | Capacity (tpa) |
|---|---|---|---|
| 1 | Jixi Liumao Graphite Resource Co. Ltd | Heilongjiang, China | 80,000-90,000 |
| 2 | Heilongjiang Aoyu Graphite Group Corp. | Heilongjiang, China | 80,000 |
| 3 | Chenzhou Luteng Crystalline Graphite | Hunan, China | 70,000 |
| 4 | Nacional de Grafite | Brazil | 70,000 |
| 5 | Karabeck Metal and Mining | Turkey | 50,000 |
| 6 | Zavalyevsky Graphite Complex | Gayvorgon, Ukraine | 40,000 - 60,000 |
| 7 | Qingdao Hensen | China | 38,000 |
| 8 | Extractive Metaquina | Brazil | 30,000 - 40,000 |
| 9 | Lubei Yxiang Graphite | China | 30,000 |
| 10 | Jilin Graphite Industry | China | 30,000 |
| 11 | Qingdao Heilong | China | 30,000 |
| 12 | Luobei Yiyang | China | 30,000 |

## APPLICATIONS

In general, natural graphite is mainly used for refractories, batteries, friction products, lubricants and the other miscellaneous, as shown in **Figure 13**.

- Refractories. Due to the high temperature stability and chemical inertness, graphite is a good candidate as refractory material for the steelmaking industries and foundry industries. Flake graphite is primarily used in the production of magnesia-carbon bricks (MgO-C), which are used as lining material in basic oxygen furnace (BOF) and electric arc furnaces (EAF) as well as in high wear areas in ladle slag lines. The bricks consist of fused magnesia and flake graphite (15-25%) bonded with synthetic resin. For this purpose large flakes (>150 micrometer) with a carbon content of at least 85% are preferred. Graphite is also an important material used in the production of functional refractories for the continuous casting of steel. In this application graphite flake is mixed with alumina and zirconia and then isostatically pressed to form components such as stopper rods, subentry nozzles and ladle shrouds used in both regulating flow of molten steel and protecting against oxidation. In blast furnaces graphite blocks are

used to form part of the lining. In many electrical metallurgical furnaces (such as EAF) the electrodes are manufactured from graphite. Graphite is also used to manufacture crucibles, ladles and moulds for containing molten metals.
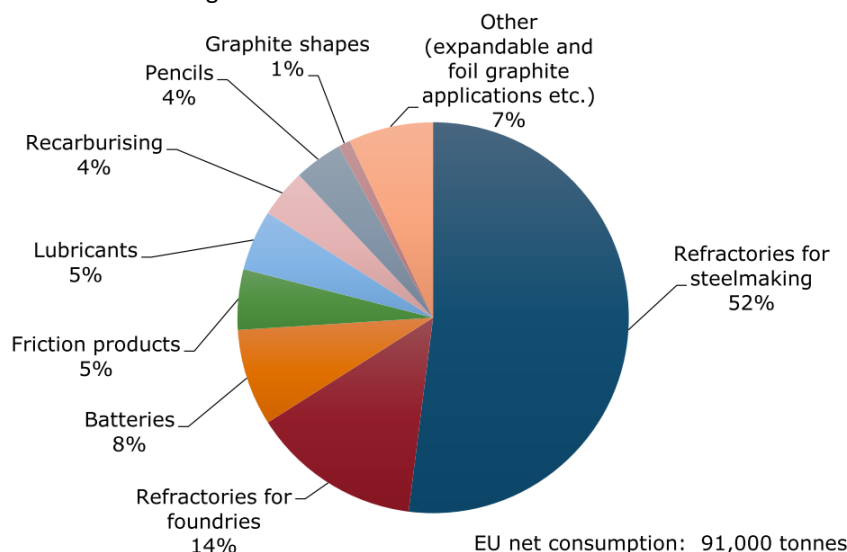


**Figure 13** Global uses of natural graphite in 2014.[1]

- Batteries. Graphite is used in the zinc-carbon batteries and more recently in the lithium batteries for its conductivity. For such applications, both synthetic graphite and natural graphite (flake graphite) can be used. Manufacturers preferred to use synthetic graphite because of its superior consistency and purity to natural graphite. This is changing and with modern chemical purification processes and thermal treatment, natural graphite can achieve a purity of 99.9% compared to 99.0% for the synthetic equivalent. The use of natural graphite for lithium battery is more economic.[5]
- Friction products. Natural graphite has high thermal conductivity for heat dissipation. It is added to friction products, such as brake linings, brake pads and clutch facings, to provide lubrication and increased thermal transfer in order to improve operation at higher temperatures.[1]
- Lubricants. Graphite possesses exceptional lubricating properties, which make it highly suitable for use in lubricants. Its applications include the use in heavy machinery to reduce friction between parts where high temperatures prevail, such as in sliding bearings, piston rings, guide bearings and steam joint rings, sliding and sealing rings for mechanical seals, vacuum pumps, compressor and pumps.[6]
- Recarburizer. Natural graphite is also used to carbonize the metals.
- Pencils. Pencils are made from natural graphite mixed with clay. Graphite is suitable for this application because the weakly held layers of carbon atoms slide easily over each other and allow for a black streak to be left on paper. [6]

## 17.2 PROCESSING TECHNIQUES RECOGNITION AND ANALYSIS

### 17.2.1 MINING

Natural graphite can be mined by both open pit and underground mining methods. Open pit mining involves extracting rock or minerals from an open pit or burrow. Drilling and blasting methods are common methods used

to liberate large-sized graphite flakes. Underground mining is done when the ore is present at a greater depth. Drift mining, hard rock mining, shaft mining and slope mining are methods used for underground mining.[7], [8]

## 17.2.2 MINERAL PROCESSING

The mineral processing of natural graphite may vary from a complex four-stage flotation (e.g. mills at Europe and United States) to simple hand sorting and screening of high-grade graphite ore at Sri Lanka. A typical processing flow-sheet of processing natural graphite is shown in **Figure 14**. The key steps for the processing include comminution (crushing, grinding, etc.) and flotation.[9]

- Comminution. Size and grade are two important parameters of graphite products for commercial considerations. On one hand it is the best to maximize the amount of large particles (flakes) and minimize the comminution steps. One the other hand, proper comminution is required to liberate the gangue minerals and impurities. Therefore, the comminution of natural graphite varies with the type of the ore to be processed.
- Flotation. Graphite is naturally hydrophobic, thus it can be upgraded by flotation. As for natural graphite, surfactants and depressants are normally added to improve the flotation process. In general, graphite flotation is carried out by combining a simple rougher flotation stage with several stages of cleaning flotation. Fine graphite can be upgraded to about 95% carbon by flotation.
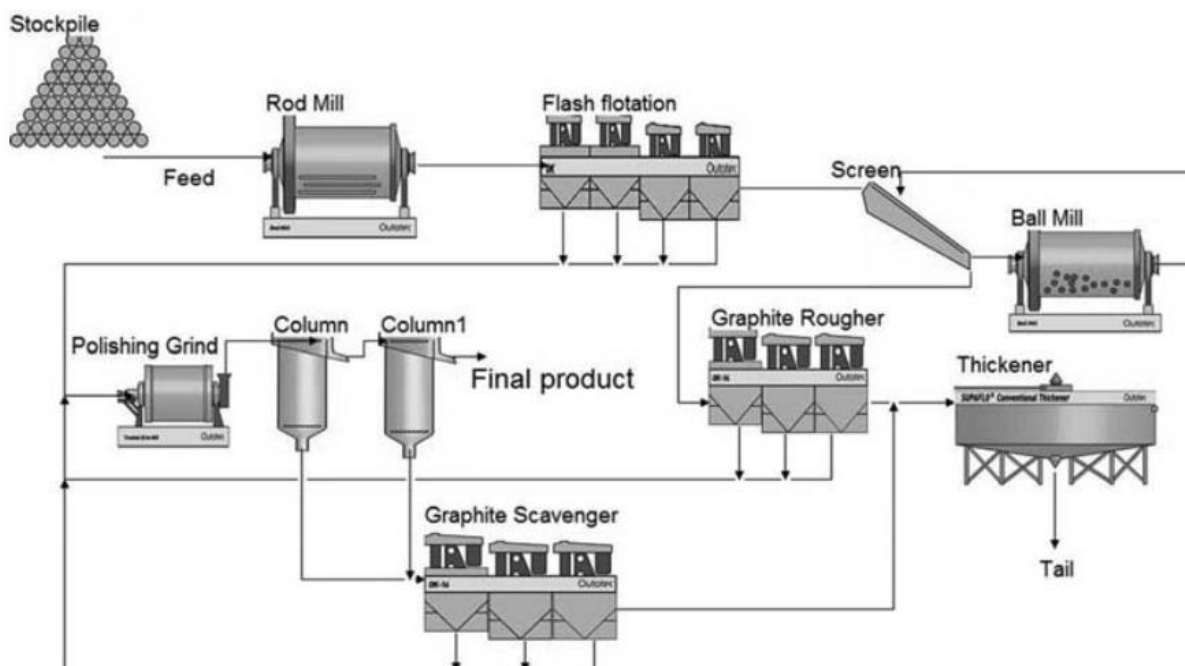


**Figure 14** Typical flowsheet of processing natural graphite.[9]

## 17.2.3 REFINING

The graphite concentrate normally are treated by chemical methods to produce the high purity graphite. The common processes for refining of graphite concentrate include acid leaching and roasting.[9]

- Acid leaching is the most common technique to refine the natural graphite after flotation. The common used acids include HCl, HF, $H_2SO_4$, $HNO_3$ or even mixtures of them. The type of the acid to be used is dependent on the type of the impurities in the graphite. Sometimes, acid leaching is also taken as a pretreatment before floatation, as the leaching process reduce the contents of impurities in the graphite and thus increase the hydrophobicity of the graphite. Acid leaching is an effective way to remove silicate impurities, while the products usually contain too much sulfidic sulfur, which needs to be removed by additional refining process.
- Roasting-leaching is an effective way to eliminate both silicates and sulfides from the graphite concentrates. The roasting-leaching process normally consists of roasting, water washing and then acid leaching. According to the literature, treatment of 1 ton graphite concentrate needs 450-500 kg NaOH and requires numerous steps of digestion, washing and drying of the graphite. The roasting-leaching process can produce graphite with 99.99% carbon. The main drawbacks of this process are the generation of a large quantity of acidic and alkaline waste water.

## 17.3 VALUE CHAIN, IDENTIFICATION OF SECONDARY RESOURCES AND LOSS OF GRAPHITE INTO THE ENVIRONMENT

According to the primary flow of the natural graphite, the primary value chain of the natural graphite can be drawn, as shown in **Figure 15**, in which the secondary resources of natural graphite and the loss of graphite into the environment can be identified.

(1) Tailings and middling. These materials are generated during the mineral processing of the natural graphite ore. A part of the graphite in these materials can be recovered by multi-stage grinding and flotation. However, it is believed that some of them are lost into to the residual materials or, even worse, dumped as wastes.

(2) Residuals from the refining process. During the roasting-leaching processing, some graphite is lost in the residual materials. There is no open information found regarding recover of the graphite from these residual materials.

(3) End-of-life products. The use of graphite in the products is dissipative in quite many cases, such as the use of graphite for producing lubricant and pencils. At moment only the recovery of graphite from refractories, foundries and batteries seems to be practical.[3], [10]
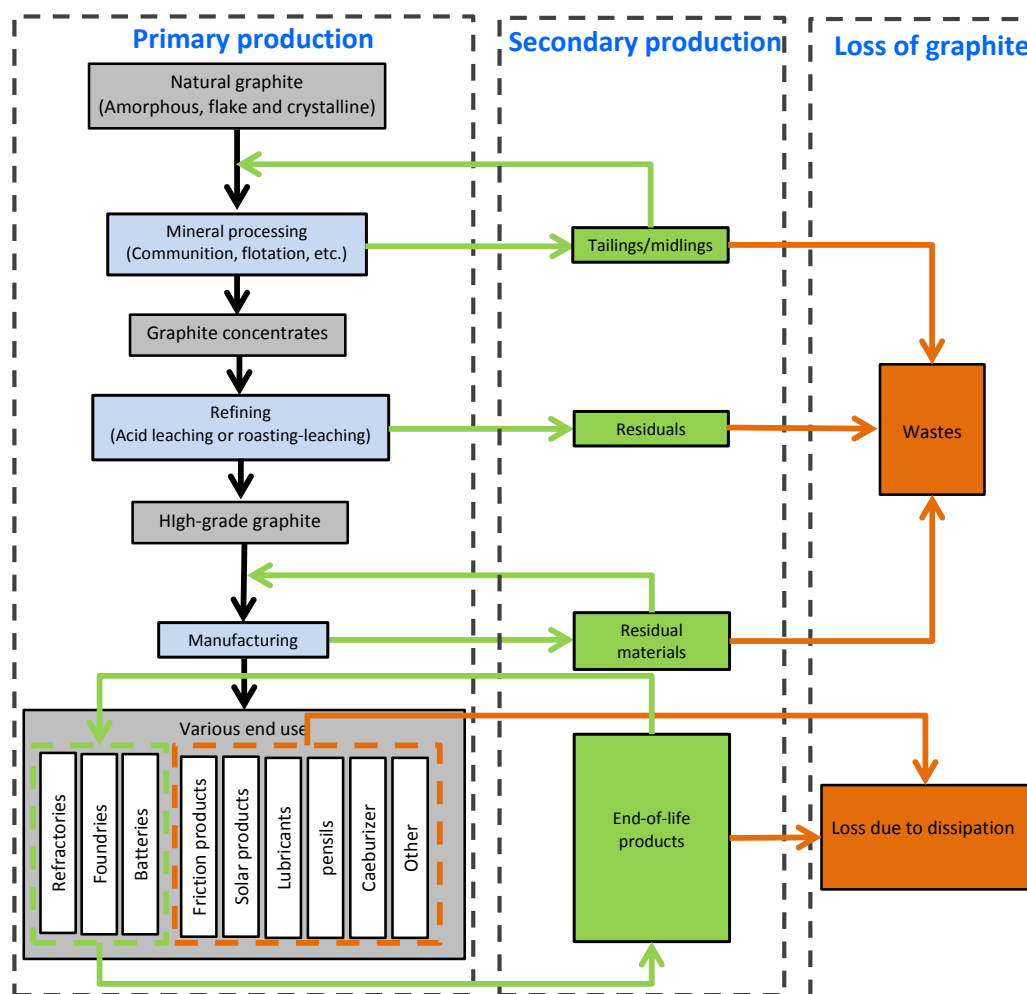
**Figure 15** Value chain of natural graphite.

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# 18  NATUAL RUBBER

Natural rubber is primarily harvested from the rubber tree Hevea brasiliensis mainly in South-East Asia. The tire industry is the largest consumer of natural rubber, accounting for around 75% of annual demand. Use of natural rubber in European value chains is dominated by the tire industry, whereas in Asia the General Rubber Goods (GRG) applications in high-tech industries play an important role. There are many uncertainties in natural rubber production for both end-user and producer, given the biotic nature of the raw material. (European Commision 2017)

## 18.1 PROCESSING TECHNIQUES RECOGNITION AND ANALYSIS

### 18.1.1  CHALLENGES RELATED TO NATURAL RUBBER PROCESSING

BIOLOGICAL CHALLENGES

As a biotic material, natural rubber is at risk from biological threats, namely plant diseases. This is especially the case with Hevea brasiliensis, since it is genetically very homogeneous: all commercial rubber tree plantations are derived from a small sample of seeds. The risk from plant diseases has already been realised once, as in 1934, a plant disease called South American leaf blight (SALB) devastated the natural rubber production in Brazil. The production in Brazil has remained marginal since then. Accidental spread of SALB in South-East Asia could reduce the natural rubber production by millions of tons in a timescale of some years, leading to serious shortages, and consequently drastically higher prices. (van Beilen 2006) Rubber plantations can also be damaged by natural disasters such as typhoons. (ANRPC 2017)

There area also other threats to natural rubber production, including competition for land by palm oil plantations. For example, the palm oil acreage in Malaysia increased from less than 100,000 hectares to almost 2,000,000 hectares in only three decades. Currently the palm oil acreage is more than the rubber tree acreage, and together the two crops account for more than 70% of the total agricultural land use of Malaysia. Similar development is occurring in Thailand and Indonesia. (van Beilen 2006)

ECONOMICAL CHALLENGES

As latex harvesting is very labour-intensive, the labour costs can also become an issue. This is an important matter especially in Malaysia, as the Malaysian economy is shifting to an industrial basis. In addition, the effects of climate change, pollution, economic development, and population growth are partly unpredictable factors possibly inducing major changes in available acreage, yield, and demand for natural rubber, as with all agricultural commodities. (van Beilen 2006)

ENVIRONMENTAL CHALLENGES

The processing of natural rubber requires large amounts of water. This water is mostly taken from underground aquifers, lakes, canals, or rivers. On the whole, the water consumption of plants processing 100-200 t of dry rubber per day is estimated to be between 3000 and 8000 m³/day. The variation arises from the need to adapt processes to the non-consistency and contamination levels of the local raw material. (Biénabe et al. 2017)

In general, rubber from Hevea brasiliensis needs rather limited processing, basically drying or stabilisation of the latex. (van Beilen 2006) However, a waste stream referred to as natural rubber waste serum (NRWS) is formed

when concentrated latex is produced. The principal method for producing concentrated latex is by centrifugation, which separates the latex into two phases: the upper cream latex phase (constituting 40 vol-%) and the lower skim latex phase (constituting 60 vol-%). The upper phase is the concentrated latex containing about 60 m-% of dry rubber, while the lower phase only contains a small percentage of dry rubber. To recover this, sulphuric acid is usually added to the skim latex phase to coagulate the rubber. The clearer part forms the NRWS, and is discharged into wastewater treatment ponds. (Pake et al. 2015) The NRWS contains many hazardous substances and its pH is low. (Abraham et al. 2009)

There are many technologies applied for the treatment of rubber latex wastewater, such as decantation, settling and filter, and anaerobic digestion. However, several limitations still exist in the used treatment technologies, the main challenge being the low efficiency. (Nguyen & Luong 2012) A sustainable treatment of the NRWS has been under investigation in many studies, including electrochemical treatment (Abraham et al. 2009), anaerobic co-digestion with macroalgae (Pake et al. 2015) and radiation treatment (Abraham et al. 2017)

## 18.1.2 PROCESSING METHODS

Natural rubber is an elastomeric hydrocarbon polymer, which occurs as a milky emulsion known as latex in the sap of rubber trees. Chemically natural rubber is cis-polyisoprene. The natural rubber production begins with tapping, where the tree is wounded in a controlled way and the latex extracted, as seen in Figure 16. The production of latex from one tree in a day is about half a cup, which consists of 30-35% rubber, the rest being water. The rubber content may vary widely with the age and the species of the tree. Trees provide the highest yields in the first five years of tapping, which can be started when the tree is 7-8 years old. (Rani 2013)



Figure 16. Tapping of rubber trees. (Picture by Joe Zachs, licence CC BY 2.0)

Natural rubber is collected from the field both as latex and field coagulum. Latex accounts for 70-80% and the rest is field coagulum. The field coagulum is composed of various tapping residues, such as remains of the latex in the cup and on the tapping cut, in addition to so called earth lump, which is formed of the small amount of coagulated latex spilt on the ground. Some specific products are made of the field coagulum. (Rani 2013)

The latex from the collection cup is poured in buckets, which are always kept exposed to sunlight. Latex has a tendency to undergo pre-coagulation in 4-6 hours. Pre-coagulation during storage can be prevented by the use

of anti-coagulants such as formalin, ammonia and sodium sulfite. The tapped latex should not be contaminated with bacteria, so it is crucial that good hygiene is maintained in the field with all tools used. (Rani 2013)

Next, the latex is converted to marketable forms, which include (Rani 2013):

- Ribbed sheets
- Crepe rubber
- Technically specified rubber (TSR)
- Latex concentrates

The following processing steps depend on the product form. For ribbed sheets the procedure involves sieving, bulking, addition of necessary chemicals, coagulation dripping, sheeting and drying. The drying method, which can be for instance air, sun, or smoke based, determines the type of the product. (Rani 2013) For instance, RSS refers to ribbed smoked sheet, which is further divided in several grades with different specifications. (Namazie International 2014a) The simplified process flow chart for making RSS is shown in Figure 17.
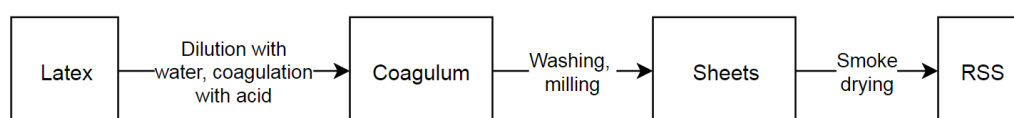


Figure 17. Flow chart for the processing of RSS.

Crepe rubber products include pale latex crepe (PLC) and sole crepe, which require high quality latex. The production process involves sieving and bulking, addition of chemicals, removal of pigments, fractional coagulation, bleaching, coagulation crepe making and drying. The machine for crepe making consists of two coarse macerators, an intermediate macerator and three sets of smooth plane rollers. The sole crepe is made by piling up a required number of PLC layers, after which the stack is warmed to a temperature of 45 °C and passed through the laminating rollers. There are also crepe products made of field coagulum. (Rani 2013)

TSR can be produced both from latex and field coagulum. For a latex-based product, the production steps are latex sieving, bulking, coagulation, passing the rubber through the crepe making machine, drying and converting to bales. When the used raw material is field coagulum, the procedure involves soaking the material in water to remove impurities and them breaking the coagulum into small pieces using a hammer mill. Next, the coagulum is dried in an oven and made into bales. (Rani 2013)

TSR, also known as block rubber, is graded according to technical parameters such as dirt content, ash content, nitrogen content, volatile matter and the material properties of the rubber. The TSR grades most widely used by the tyre and rubber industry are the TSR-20 and TSR-10. (Namazie International 2014b) A process flowchart for the manufacture of TRS-20 is shown in Figure 18.
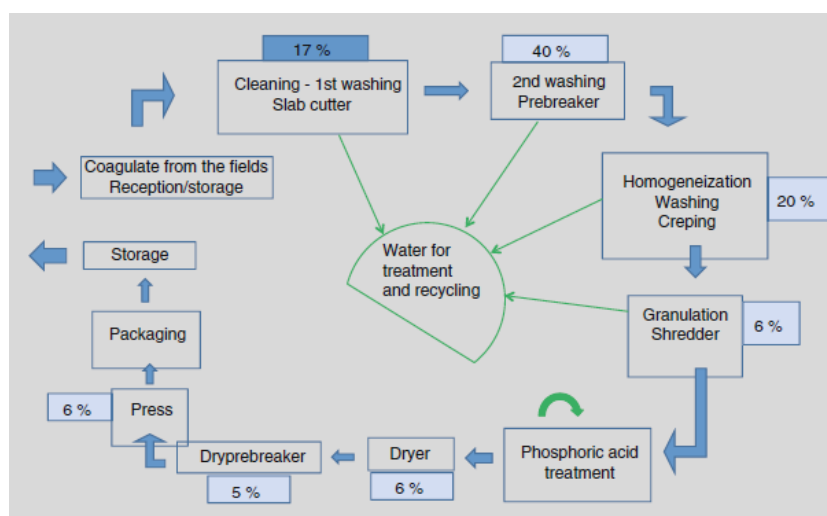
Figure 18. A process flowchart for TSR-20 rubber production. The share of installed power requirement for each sub-process is shown in the light blue boxes. Reproduced from (Biénabe et al. 2017).

Around 10% of the supply of rubber is delivered in the shape of latex (European Commision 2017). As the fresh latex obtained from the plantation is not suitable for storage and marketing as such, it has to be processed to make it suitable for further use. The most important processes for this purpose are preservation and concentration. For preservation, usually ammonia is used. It prevents both spontaneous coagulation and putrefaction. Concentration of latex is necessary because of the preference for high rubber content by the manufacturing industries, economy in transportation and a higher degree of purity. The concentration methods are centrifuging, evaporation, electro-decantation, and creaming. (Rani 2013)

## 18.1.3 INDUSTRIAL ACTORS

The world's largest natural rubber manufacturers are mainly located in Southeast Asia. Among them, Sri Trang Agro-Industry is the world's largest natural rubber producer with sales volumes accounting for 11.9% of the global total consumption in 2016. (Business Insider 2017) Some of the largest natural rubber produced are compiled in the following table.

Table 6. Some of the largest natural rubber producers. (Business Insider 2017)

| Company | Country | Capacity | Reference |
|---|---|---|---|
| Sri Trang Agro-Industry Public Co.,Ltd (STA) | Thailand, Indonesia, Myanmar | 2.4 Mt/year | https://www.sritranggroup.com |
| Von Bundit Co.,Ltd. | Thailand | 1.8 Mt/year | http://www.vonbundit.com |
| Southland Rubber | Thailand | 168 kt of latex concentrates/year + RSS and STR | http://www.southlandholding.com |
| China Hainan Rubber | China | 210 kt of dry adhesive/year | http://www.rubbervalley.com/english/ArticlePage.aspx?class1=2&class2=17&id=17 |
| Guangdong Guangken Rubber Group Co. | China | processing capacity of 1.5 Mt/year | http://www.chinadaily.com.cn/business/2016-11/28/content_27500097.htm |

| Halcyon Agri Co.,Ltd. | Singapore (Indonesia, Malaysia, Thailand, China and Cameroun) | 2 Mt of aggregate natural rubber/year | https://www.halcyonagri.com/ |
|---|---|---|---|
| St. Mary's Rubbers Pvt. Ltd | India | 73 kt of field latex/year | http://www.stmarysrubbers.com |

A comprehensive list of natural rubber producers is compiled by the Association of Natural Rubber Producing Countries (ANRPC). (ANRPC 2014)

## 18.2 PROCESSING OF THE RESIDUES

The field coagulum can be considered as a processing waste, which is completely utilised as a raw material. Other recoverable processing waste streams could not be identified. The rubber trees are used to make furniture and souvenirs at the end of the trees' useful life (AZoM 2006).

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# 19  PHOSPHATE ROCK

Phosphate rock refers not only to unprocessed rocks containing about three hundred phosphate minerals, usually calcium phosphate as apatite with the formula $Ca_5(PO_4)_3(F,Cl,OH)$, but also to beneficiated concentrates. (European Commision 2017; Van Kauwenbergh 2010). 80-85% of phosphate rock is mined from sedimentary deposits and the rest mainly from igneous deposits. Large sedimentary deposits are located in China, the Middle East, northern Africa and the United States. Igneous deposits are mined in Brazil, Canada, Finland, Russia, South Africa and Zimbabwe. (Jasinski 2013; Scholz et al. 2014)

The processing paths for various phosphate-based products is presented in the following figure.
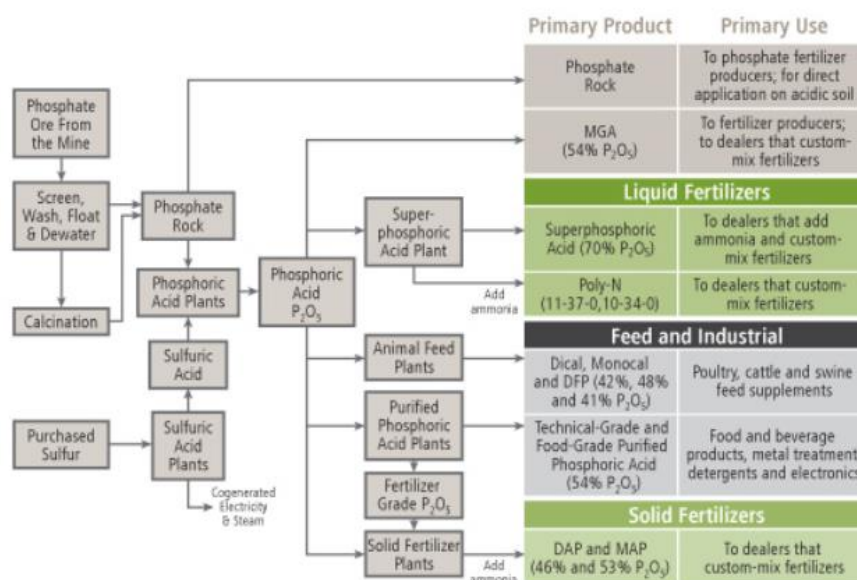


Figure 19. Processing paths of phosphate fertilisers and other phosphate-derived products. Reproduction from (PotashCorp 2014).

## 19.1 PROCESSING TECHNIQUES RECOGNITION AND ANALYSIS

Surface method, see Figure 2, is the most common way to mine phosphate rock: In 2013, only one underground mine was active in the world. (Jasinski 2013) Marine dredging has also been examined, for example off the coast of Mexico, the Eastern coast of the United States and currently off the Namibian coast. (Scholz et al. 2014)

Especially in the U.S., public opposition to phosphorus mining is on the rise due to possible environmental and health effects related to phosphate mine tailings. In addition, heavy metals passing through to phosphorus fertilizers originating from some phosphate ores has raised concern. Therefore, phosphorus mining in Florida, where the largest deposits of phosphorus are found in the U.S., is being challenged about its effects on waterways and drinking water supplies. For example, the Florida South Fort Meade phosphorus mine has faced opposition to its expansion for this reason, and is at risk to have to close if it cannot develop. (Vella 2016)

Figure 2. A phosphate rock surface mine in Israel. (Public domain)

## 19.1.1 MINERAL PROCESSING

Phosphate ores may have a grade anywhere between 5 and 39 % of P2O5. Beneficiation plants are commonly combined with the mine. After extraction, phosphate ore typically undergoes a process of concentration, which may include primary screening, wet or dry screening, washing, flotation, magnetic separation and drying to produce, in commercial terms, phosphate rock concentrate. The P2O5 level in the concentrate typically ranges in 28-40%. (Scholz et al. 2014) Moroccan phosphate rock concentrate of 32%-33% P2O5 FOB is typically used as the benchmark for worldwide phosphate pricing. (GBMinerals 2015)

Phosphate rock may be transported to a port for export or a domestic plant for direct use or further downstream processing. However, only a limited amount of phosphate rock is sold or used without primary processing. Transportation of the ore, in the form of slurry, is usually managed by trucks, railways, conveyor belts, or pipelines. (Scholz et al. 2014)

The recovery efficiency of mining extraction averages 82% for the 93% of the world phosphate producers. However, two-thirds of producers operate above this weighted average ratio. (Scholz et al. 2014) There are several methods to beneficiate phosphate rock, and usually a combination of methods is used. (Van Kauwenbergh 2010)

In phosphate rock beneficiation, the availability of water is essential and may dictate the process or processes to be used. The total lack of (fresh)water availability may exclude deposits from development or restrict capacity. In areas where water availability is severely restricted, dry screening may be an effective way to produce concentrates or pre-concentrates if ore characteristics are suitable. Seawater can be used for washing, size classificatior, and flotation. Where other than freshwater is used for beneficiation, a freshwater final rinse is needed to remove as much chloride as possible from the final concentrate, since a high chloride content can lead to severe corrosion in further processing. (Van Kauwenbergh 2010)

### 19.1.1.1    SILICEOUS SEDIMENTARY PHOSPHATE ORES

As mentioned above, sedimentary phosphate deposits account for approximately 80% of the world's total phosphate rock production. Many of the world's largest phosphate reserves, such as those in Florida, Morocco, and China, are sedimentary phosphates. Sedimentary phosphates are usually formed of small pellets, of which size ranges from fine sand to larger pellets. Some forms of francolite or collophane are characteristic minerals in these deposits, whereas typical gangue minerals include clays, silica, calcite, and dolomite. Traditional high-grade reserves contain mainly clays and silica, and are therefore referred to as siliceous phosphate ores. These types of ores can be processed relatively simply and efficiently by methods that include sizing or desliming and flotation. (Kawatra & Carlson 2014)

Sedimentary phosphate ore is typically mined using draglines, made into a slurry, and transported by pipelines to the washing plant. Washing is often carried out using rotating drums (trommels), log washers, and sandwich screens. The washed slurry is then sized and deslimed in preparation for the Crago double float process, which is discussed below. The simplified process flow diagram of a washing plant is presented in Figure 1. As can be seen, the -16 mesh (-0.1 cm) size fractions from the vibratory screens are conveyed to the flotation circuit. The +16 mesh size fraction from the final vibratory screen is considered to be pebble product if it contains less than 1% of MgO. If the MgO content is greater than 1%, further processing is needed to remove dolomite. (Kawatra & Carlson 2014)
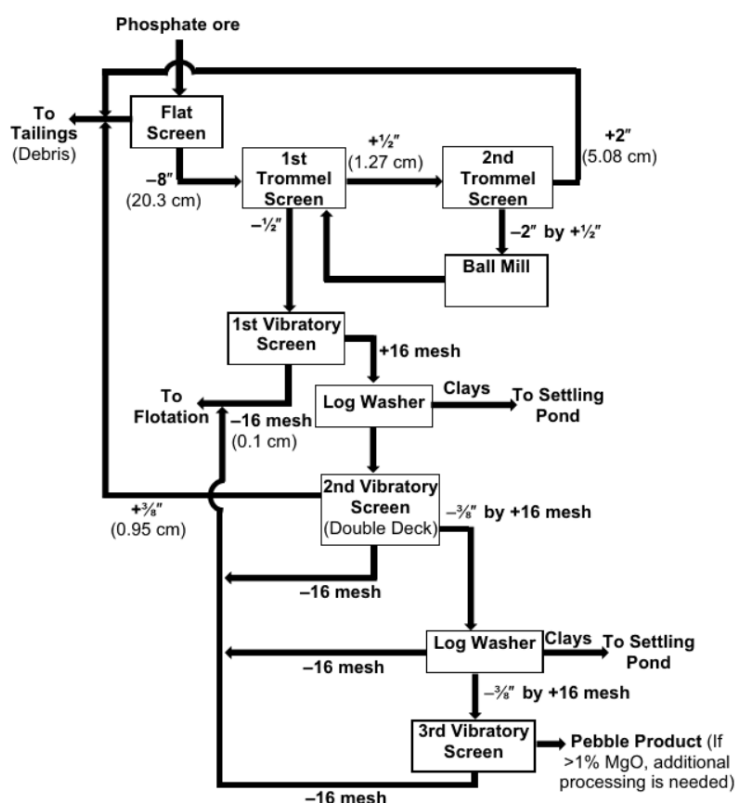


Figure 3. Process flow sheet of a phosphate ore washing plant. The output of this process feeds the Crago double float process. Reproduction from (Kawatra & Carlson 2014).

Since being patented in 1942, the Crago double float process has been the industry standard for the beneficiation of siliceous phosphate ores. The two floating processes of the Crago double float process are (Kawatra & Carlson 2014):

1. Rougher flotation: Phosphate is floated from coarse silica using an anionic fatty acid collector, and
2. Cleaner flotation: fine silica is floated from phosphate concentrate using a cationic amine collector.

The process flow sheet of the Crago double float process is presented in Figure 4. As the efficiency of this process depends heavily on a properly operated washing and conditioning steps, there are a few important process considerations (Kawatra & Carlson 2014):

- Desliming: Clays decrease the flotation efficiency and increase the reagent consumption.
- Sizing: Sizing allows for more efficient use of collector and better selectivity during anionic flotation.
- Conditioning: High percentage of solids increase phosphate grade and recovery during anionic flotation.
-
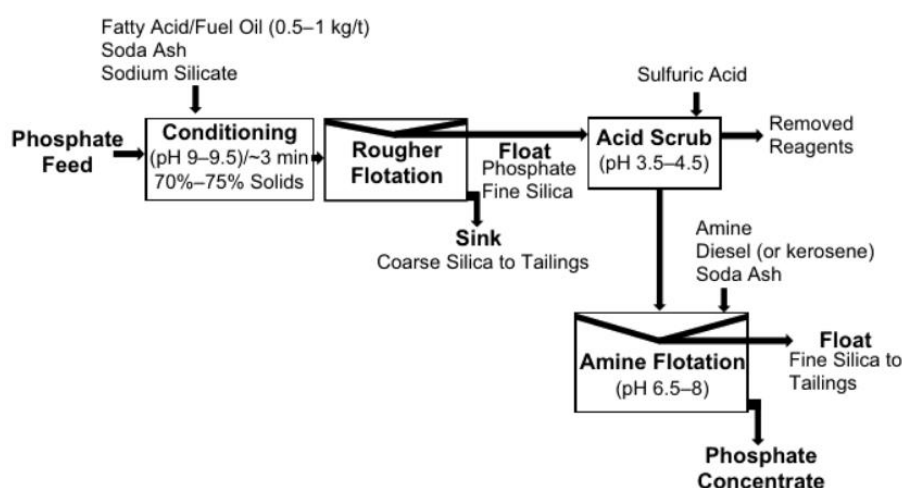


Figure 4. Process flow sheet of the Crago double float process.  Reproduction from (Kawatra & Carlson 2014).

As companies are being forced to mine and process lower-grade phosphate deposits, companies have begun to re-evaluate the efficiency of the traditional Crago process. It has been recognised that in terms of collector efficiency, the Crago double float is inefficient because the fine silica is floated twice. This has led to the development of three alternative processes: the reverse Crago process (Zhang et al. 1997), the all-anionic process, and the all-cationic process (Salah et al. 2011). However, these processes are still at developmental stages and need further evaluation to determine whether they can be commercially exploited. (Kawatra & Carlson 2014)

## 19.1.1.2   SEDIMENTARY PHOSPHATE ORES WITH HIGH MAGNESIUM OXIDE CONTENT

When treating sedimentary phosphate ores with high MgO content (MgO > 1%), resulting from significant levels of dolomite (CaMg(CO3)2) in the ore, the beneficiation process becomes more complex because of the similar mineralogical properties between the phosphate and carbonate minerals. Several techniques have been developed for the beneficiation of high-MgO sedimentary phosphate ores, but viable technologies for processing such ores on an industrial scale do not exist (Gharabaghi et al. 2010). Some of the most practical and advanced methods are presented in Table 1. (Kawatra & Carlson 2014)

Table 1. Processes developed for the beneficiation of high-MgO sedimentary phosphate ores. Adapted from (Kawatra & Carlson 2014).

| Process | Advantages | Disadvantages | Other remarks | Industrial examples |
|---|---|---|---|---|
| **Organic acid leaching** | • Good selectivity<br><br>• Lower phosphate losses than with strong inorganic acids | • Organic acids relatively expensive<br><br>• Recovery of the organic acid may be challenging | The smaller the particle size, the higher the efficiency. However, too fine sizes can impede the filtration of the phosphate concentrate. | No industrial examples available. |
| **Thermal decomposition (Calcination)** | • Complete removal of carbonates<br><br>• Low water demands | • Energy intensive<br><br>• Concentrate reactivity lower (in phosphoric acid production)<br><br>• High capital costs | Produces a phosphate concentrate suitable for the production of high-grade defluorinated phosphoric acid. | Mainly used for reducing the organic content of phosphate rock. However, in Djebel Onk, Algeria, the calciners are used for carbonate removal. (Abouzeid 2008) |
| **Heavy-media separation (HMS)** | • Capable of processing coarse feed sizes<br><br>• Relatively high throughput | • Low selectivity | HMS is usually proposed as a preconcentrating process that needs further processing to produce a saleable product. | A HMS plant was installed at Four Corners Phosphate Mine, U.S. in 1991, and by that time it was the only such plant in the phosphate mining industry. (EPA 1994) No recent information was available. |

### 19.1.1.3   IGNEOUS PHOSPHATE ORES

15%-20% of the world's phosphate production comes from igneous phosphate ores, which differ significantly from the more abundant sedimentary deposits. The majority of the igneous deposits around the world are found in southern Brazil, South-East Africa, Finland, Sweden, and Russia. The predominant mineral in these deposits are well-formed apatite crystals. Igneous phosphate rocks are typically of three types: carbonatite, nephelinic-syenite, and pyroxenite. Each of these types of deposits can vary notably in gangue minerals, but all of them are rich in fluorapatite ($Ca_5(PO_4)_3F$). (Kawatra & Carlson 2014)

The types of impurities determine the needed beneficiation methods, which can therefore range from a relatively simple flow sheet to a more complicated one. However, the common process to all igneous phosphate concentrator flow sheets is the anionic fatty acid flotation of apatite. Other processing techniques such as magnetic separation (iron removal), copper flotation, calcite flotation, and barite flotation are

implemented when needed. In some cases, these processes can generate valuable by-products. (Kawatra & Carlson 2014)

## 19.1.2 MAIN INDUSTRIAL ACTORS

As well as the US, the majority of phosphorus comes from North Africa (Morocco and Tunisia) and the Middle East (Egypt and Jordan). North Africa and the Middle East produce around 75% of the world's phosphate. There are well-established geopolitical concerns about the location of the majority of phosphorus reserves. There are also regions with untapped reserves, notably Quebec, Florida, Kazakhstan and Togo, as well as Brazil, where Vale and Anglo American each hold significant phosphate interests.

Public resistance to phosphorus mining is also on the rise, especially in the US. Some phosphate ores have significant amounts of cadmium, a contaminant which can be passed through to the final phosphorus fertilizer. Phosphate mine tailings are also known to contain uranium, which leads to radon release. These kinds of environmental concerns are behind public opposition to new mines. Phosphorus mining in Florida, where the largest deposits of phosphorus are found in the US, is being challenged by environmentalists concerned about its impact on waterways and drinking water supplies. For example, the Florida South Fort Meade phosphorus mine is currently facing opposition to its expansion for this reason, and will have to close if it cannot develop.(Vella 2016)

The price of phosphorus is not expected to bound ahead due to rather large supply, but is likely to follow the trends of potash and nitrogen and increase as demand evolves. On the other hand, there are concerns that the phosphate rock producing countries, which are currently rather small in number, would form an alliance to control the price of phosphorus. (Vella 2016)

The most relevant industrial actors beneficiating phosphate rock are listed in the following table.

Table 2. Some of the largest industrial actors beneficiating phosphate ores.

| Company | Mine site (location) | Reference |
|---|---|---|
| **Vale** | Bayóvar (Sechura, Peru) | http://www.vale.com |
| | Catalão (Goiás, Brazil) | |
| **OCP** | Benguérir, Morocco | https://www.mining-technology.com/ projects/benguearir/ http://www.ocpgroup.ma |
| | Youssoufia, Morocco | |
| | Khouribga, Morocco | |
| | Boucraâ, Western Sahara | |
| **Mosaic Co.** | Four Corners (Florida, US) | http://www.mosaicco.com |
| | South Ford Meade (Florida, US) | |
| | South Pasture (Florida, US) | |
| | Wingate Creek (Florida, US | |
| | Hopewell (Florida, US) | |
| **China Molybdenum Co. Ltd** | Chapadão (Goiàs, Brazil) | (AngloAmerican 2016) |
| **Sinochem Yunlong Co., Ltd.** | no data | (Sinofert 2016) |
| | Aurora (North Carolina, US) | https://www.mining-technology.com/projects /aurora-phosphate-mine/ |

| Nutrien (merger of Agrium and Potash Corp.) | Dry Valley (Idaho, US) | https://www.kiewit.com/projects/mining/contract-mining/dry-valleyno-rasmussen-ridge-mines/ |
|---|---|---|
| | Swift Creek (Florida, US) | (Jasinski 2016) |
| P4 Production, LLC. | Blackfoot Bridge (Idaho, US) | (Jasinski 2016) |
| Foskor | Phalaborwa (South Africa) | (Foskor 2016) |
| Yara | Siilinjärvi (Finland) | (YARA 2013) |
| Apatit | Kola, Russia | (Van Kauwenbergh 2010) |
| EuroChem | Kovdorskiy GOK (Russia) | http://www.eurochemgroup.com/en/project/kovdorskiy-gok-expansion/ |

## 19.2 PROCESSING OF MINE TAILINGS AND RESIDUES

The industrial scale processing of mine tailings and residues seems to be lacking at present. A comprehensive utilization of phosphate mining wastes was reported by Negm & Abouzeid (2008). They used solid waste from a phosphate washing plant as a feed, and proposed a beneficiation flow sheet that provided side stream aggregates for concrete and road paving, in addition to other side stream material for bricks and pottery. Laboratory-scale tests showed that the treatment of the coarse waste produced a final concentrate with P2O5 content higher than 30%, and over 90% recovery.

The most recent research on the subject by Alsafasfeh & Alagha (2017) highlighted that a concentrate product with a P2O5 content of 28.4% was achieved with a recovery rate of 75%. The used secondary source were tailings produced at a phosphorous production plant, and direct froth flotation was used as a beneficiation method.

### 19.2.1 CHEMICAL AND MINERALOGICAL CHARACTERISATIONS

According to Negm & Abouzeid (2008), the coarse waste produced by the crushing and screening process of phosphate production is estimated to assay 18-24% P2O5. The fine tailings in the tailing pond are estimated to contain 12-19% of P2O5.

### 19.2.2 POTENTIAL UTILIZATIONS

In addition to upgrading the phosphate-containing waste for phosphate industry, other potential reuses of phosphate waste rocks and tailings have been investigated during the last 10 years. These research activities have mainly been related to the reuse of phosphate mining waste as a neutralizing agent to control the acid mine drainage, or as a water infiltration material for the mine site reclamation. (Hakkou et al. 2016)

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## 20 PHOSPHORUS

### 20.1 PRODUCTION OF WHITE PHOSPHORUS FROM PRIMARY RESOURCES

A wide range of the phosphorus-based products used in chemical industry can today only be produced via elemental phosphorus $P_4$, commonly referred to as white phosphorus, but also as yellow phosphorus. These products cannot be produced from phosphoric acid. White phosphorus is produced from phosphate rock by thermal reducing. The EU has no domestic production of P4 at present. (European Comission 2017)

Elemental phosphorus is the starting material for phosphorus-containing chemicals used in a wide range of industrial markets. The most important chemicals derived directly from white phosphorus include
- phosphorus trichloride ($PCl_3$),
- phosphorus pentasulfide ($P_2S_5$ or dimer $P_4S_{10}$),
- phosphorus pentoxide ($P_4O_{10}$), and
- sodium hypophosphite ($NaPO_2H_2$).

The latter is a relatively small-volume chemical used primarily in electroless nickel plating solutions. The former chemicals are starting materials for a large number of derivative inorganic and organic chemicals, which in turn are used in a wide variety of high-value applications. (IHS 2017)

In 2016, elemental phosphorus producers were located in China, Kazakhstan, the United States, Vietnam, and India. China accounts for the largest share at about 87% in 2016, followed by Kazakhstan, the United States, Vietnam, and India. Vietnam has significantly increased capacity in the last 10 years, and was the largest supplier to the global market in 2016. (IHS 2017)

### 20.2 PROCESSING TECHNIQUES RECOGNITION AND ANALYSIS

#### 20.2.1 PROCESSING METHOD

Elemental phosphorus manufacture is based on an electrothermal process and therefore is very energy intensive: Each tonne of produced $P_4$ requires about 14 MWh of energy. Therefore the manufacture is located in areas where comparatively cheap energy, such as hydroelectric power, is available. (ECI 2017)

The process flow sheet of the manufacture of white phosphorus is presented in Figure 1. The main starting material is phosphate rock. In addition, quartzite is used as a flux material and metallurgical coke as a reducing agent. (Zhantasov et al. 2017) The feed of phosphate rock into a furnace needs to be as uniform as possible to optimize the production efficiency. To achieve this, phosphate rock is heated, usually in a rotating calciner, which results in the fusion of small particles to form the hard agglomerates required for satisfactory furnace operation. The furnace is fed with a mixture of coke, sand and phosphate rock in a mass ratio of, typically, 16:30:100. (ECI 2017)

The reaction in the furnace at approximately 1350 °C can be represented as:

$$2\ Ca_3(PO_4)_2(s) + 6\ SiO_2(s) + 10\ C(s) \rightarrow 6\ CaSiO_3(s) + P_4(g) + 10\ CO(g)$$
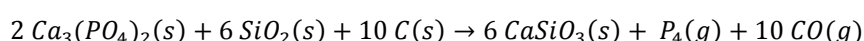
Molten calcium silicate slag and an alloy of iron and phosphorus, known as ferrophosphorus are removed separately from the base of the furnace. The ferrophosphorus can be utilised in steel-making and some quantities of calcium silicate are used as low-grade hardcore. (ECI 2017)

Gaseous phosphorus and carbon monoxide, from the top of the furnace, are purified from the dust in electrostatic precipitators and then passed into a spray of water at 70 °C. At this temperature, most of the phosphorus condenses as a liquid phosphorus. Complete condensation is achieved using cold water, where solid phosphorus is formed. The solid phosphorus is melted, combined with the liquid phosphorus from the first condensator and stored under water. The carbon monoxide can be recycled as a fuel in the preliminary heat treatment of phosphate rock. (ECI 2017; Zhantasov et al. 2017)
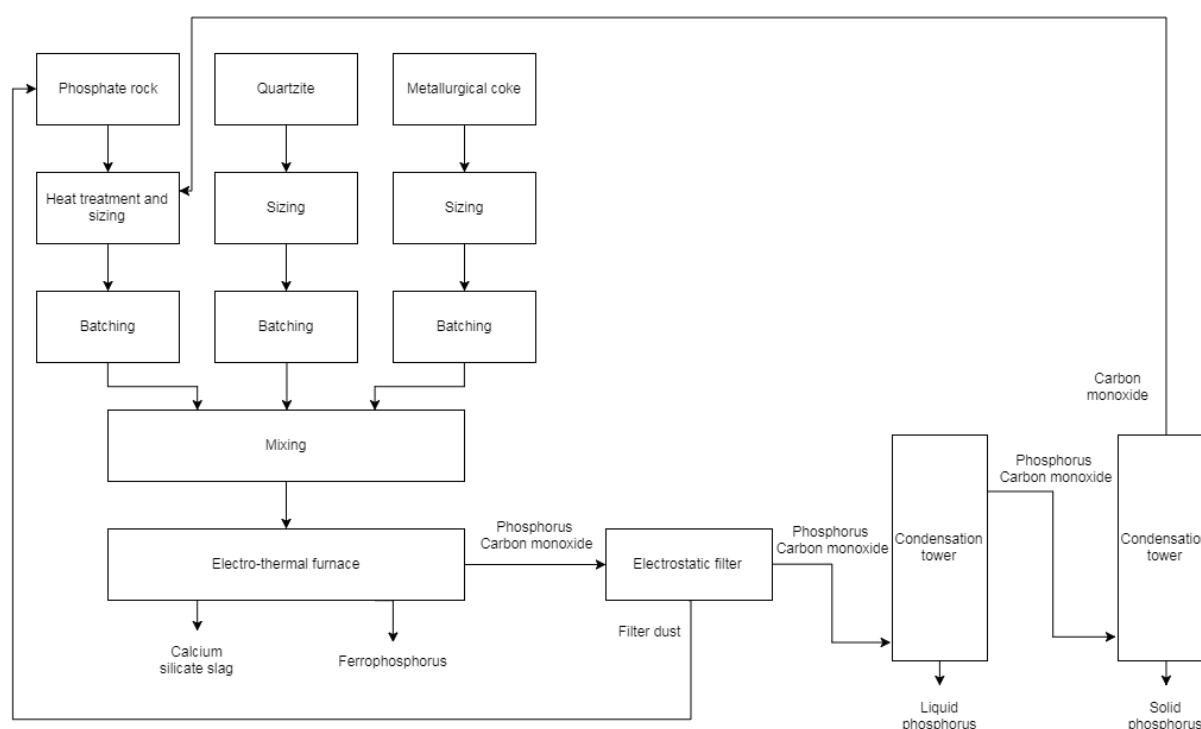


Figure 1. Process flow chart of the manufacture of white phosphorus. Adapted from (Zhantasov et al. 2017).

## 20.2.2 INDUSTRIAL ACTORS

Asia Pacific dominates the global white phosphorous market, and most of the manufacturers of white phosphorus are located in China. While demand for white phosphorus is increasing in Asia Pacific, also North America and Europe are favorable markets for white phosphorus. In addition, call for white phosphorus in Middle East and Africa too is increasing speedily; currently Saudi Arabia is a major importer of white phosphorus. (TMR 2017) The following table sums up the global industrial producers of white phosphorus.

Table 7. Some of the largest white phosphorus manufacturers. (TMR 2017)

| Plant location | Company | Reference |
|----------------|---------|-----------|
| China | Yunphos (Taixing) Chemical Co., Ltd. | |
| China | Changzhou Qishuyan Fine Chemical Co. Ltd. | |
| China | 5-Continent Phosphorus Co. Ltd. | |

| India | Taj Pharmaceuticals Ltd. | |
| India | UPL Europe Ltd. | (UPL 2016) |
| Vietnam | Viet Hong Chemical and Trading Co. Ltd | |
| Kazakhstan | Kazphosphate LLC | (Kazphosphate 2012) |

## 20.3 PROCESSING OF MINE TAILINGS AND RESIDUES

The literature doesn't acknowledge any examples of white phosphorus production from mine tailings or other residues.

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# 21 PLATINUM-GROUP METALS (PGMS)

## 21.1 PRODUCTION LINES OF IDENTIFICATION FROM PRIMARY RESOURCES

### 21.1.1 PGMS, PRODUCTION AND APPLICATIONS

The six platinum-group metals are ruthenium, rhodium, palladium, osmium, iridium, and platinum. They have similar physical and chemical properties, and tend to occur together in the same mineral deposits (Harris, D. C.; Cabri L. J., 1991). Based on their behaviour in geological systems they can be further subdivided into the iridium-group platinum-group elements (IPGEs: Os, Ir, Ru) and the palladium-group platinum-group elements (PPGEs: Rh, Pt, Pd) (Rollinson, 1993). They are also classified into two groups based on their specific gravities: the lighter PGEs including ruthenium, rhodium, and palladium, with specific gravities around 12.0–12.4, being lighter than gold; and the heavier PGEs including osmium, iridium, and platinum with the specific gravity in the range of 21–22.5, being heavier than gold (Xiao and Laplante, 2004).

In 2015 the mine productions of platinum and palladium were 178, 000 kg and 208, 000 kg, respectively. The major production countries of PGMs are South Africa, Russia, Canada, Zimbabwe and USA (USGS, 2016).

Being highly resistant to wear and tarnish PGMs are well suited for fine jewelry and other distinctive properties include their resistance to corrosion and oxidation, high melting points, electrical conductivity, and catalytic activity make them have wide industrial applications (Xiao and Laplante, 2004; Hunt and Lever, 1969).

### 21.1.2 PRIMARY RESOURCES FOR PGMS PRODUCTION

#### 21.1.2.1 PGES MINERALS AND ORES

There are 109 PGEs minerals recognized by the International Mineralogical Association (IMA), ranging from sulphides (i.e. braggite, (Pt,Pd)S) to tellurides (i.e. maslovite, PtBiTe), antimonides (i.e. sudburyite, PdSb) to arsenides (i.e. sperrylite, PtAs2), and alloys (i.e. ferroplatinum alloy) to native species (i.e. native Pt nuggets). The three main minerals associated with PGMs are pyrrhotite, chalcopyrite, and pentlandite.

The world resources of PGMs are estimated over 100 million kg and the reserves are 66 million kg. The largest reserves are in the Bushveld Complex in South Africa (USGS, 2016). The majority of current primary PGE production is derived from sulphide ores. There are two major primary resources or ores: the PGEs dominant ores and the Ni–Cu dominant ores [3] [5-7]. There are miscellaneous ores in which PGE values have been noted but not recovered due to low concentrations or recovered as a by-product with little or no economic advantage for the primary producer (Cole and Ferron, 2002-03).

The PGEs dominant ores are exploited primarily for their PGEs content, other associated metals, such as Cu, Ni and Co, produced as by-products. The economic values of the PGEs are, in general, major in comparison to the by-product values. The Ni–Cu dominant ores are mined primarily for the value of Ni and Cu. The PGEs are produced as by-products. Usually, the economic importance of PGEs in these ores is minor. However, they can, in some cases, become the very important ''deciding factors'' for project economics (Cole and Ferron, 2002-03).

The PGEs dominant ores

1)      Merensky type

In general, the Merensky type deposits are layered with disseminated sulphides. The total sulphide content is fairly low; in some cases, the PGE are associated with chromite as well as sulphides. Some examples of this type of deposit are the Merensky Reef in South Africa and the Great Dyke in Zimbabwe. The Stillwater complex is thought to be similar in nature to the Merensky type deposit. Typical grades of PGE for this type of deposit range from 3 to 20 g/t PGE.

The Merensky Reef

Mill head grades typically vary from about 4 to 8 g/t PGE + Au. The PGE occur as discrete PGM (primarily braggite, cooperite, laurite, sperrylite, moncheite and Pt-Fe alloys intergrown with base metal sulphides and in solid solution with the Cu, Ni and Fe sulphides. The principal opaque sulphide minerals are pyrrhotite, pentlandite and chalcopyrite. Typically, the PGE will occur as fine inclusions within the BMS or as intergrowths between the Base Metal Sulphides (BMS) and gangue contact surfaces, which aids liberation during the grinding process. In general, the liberation size is fairly coarse with most operations choosing a grind size (P80) between 75 and 150 µm. The presence of talc in some areas can cause significant process difficulties.

The Stillwater Complex

The production from the Stillwater complex originates from the J-M (Johns-Manville) reef. Unlike the Merensky reef where Pt is the primary PGE, Pd is the most significant PGE present in the Stillwater complex. The principal opaque minerals are pentlandite, pyrrhotite and chalcopyrite. The principal PGE are braggite, vysotskite, moncheite and Pt-Fe alloys (note the similarities with the Merensky PGE suite). The PGE vary considerably in size from 1 to 200 µm in size. Braggite and vysotskite are coarser-grained while the Pt-Fe alloys tend to be finer grained. The amount of PGE in solid solution with the base metal sulphides is variable with the amount of Pd present in pentlandite, varying from 0.04 to 1.5%. An average head grade for the mill would run at about 24 g/t PGE (Turk, 2001).

The Lac des Iles Complex

The primary PGE in the Lac des Iles complex is Pd. Major opaque minerals include pentlandite, pyrite, chalcopyrite and pyrrhotite. The most abundant PGE is vysotskite (reported to have close associations with pentlandite). Other PGM present include the braggite series of minerals, kotulskite, as well as antimonides and sulphantimondes. As with the Merensky reef, there is a fair amount of variability in the relative abundance of the PGE. Similar to the Merensky and JM reef, the PGE also occur in solid solution with the BMS, with the pentlandite containing between 0.02 and 0.65% Pd. The presence of talc in the ore is consistent with the Merensky type ore. The average mill head grade for 2000 was 4.5 g/t Pd (North American Palladium Ltd., 2001).

   The Lac des Iles Property (the Property) is located approximately 85 km northwest of Thunder Bay,

    Ontario.

The Great Dyke

The most recent publication on the Great PGE deposits is that of Oberthur (this volume). The BHP-owned mine, Hartley Platinum, was exploiting this ore body and failed because of mining problems relating to grade dilution

(no marker for the reef such as the thin chromite layers associated with the Merensky reef). The average head grades for this reef are approximately 4 g/t PGE with about 55% of the PGE content present as Pt. The Mimosa mine has been exploiting this ore body successfully for a number of years and has just expanded its operations.

2)      Chromite type

Two types of chromite deposits being economically or potentially economically significant. Stratiform chromite deposits occur in the Bushveld complex (UG2 reef, the UG, LG & MG series reefs), the Great Dyke, the Stillwater Complex (lower chromitites), and the Muskox intrusion (Northwest Territories).

The UG2 Chromite

The reef consists of 60-90% chromite, 5-25% orthopyroxene and 5-15% plagioclase with trace amounts of base metal sulphides. The primary sulphides are pentlandite, pyrrhotite, chalcopyrite and pyrite. The sulphide grains occur typically in the size range 1 to 30 µm and occur mostly in the chromite grain boundaries. This phenomenon assists in liberation of the BMS, as the ore will only need milling down to the natural chromite grain size (typically about 100 µm) in order to expose the BMS surfaces. The BMS can then be liberated by detachment. The PGM are typically associated with the BMS and will have a size ranging from 1 to 2 µm, and rarely exceeding 20 µm. The principal PGM in the UG2 reef include: malanite, laurite, cooperite, braggite, Pt-Fe alloy, sperrylite and vysotskite. The PGM may also occur as single grains along chromite grain boundaries or as inclusions within chromite or other silicate gangue minerals (Cabri, 1981b).

The Lower Chromitites, Stillwater Complex

Although mineralogical studies have shown the presence of PGM and BMS within these rocks it is unlikely that they will ever be economically exploited. The chromite (Cabri, 1981b; Zientek et al., 2002) and olivine thus not amenable to recovery by flotation unless very fine grinding is employed to liberate these minerals. It is likely that the grinding costs associated with the process will make the economics of the project unfavourable. Podiform chromite deposits are mined primarily for their metallurgical grade chromium content. These chromitites may be enriched in Os-Ir-Ru alloys. In the future, recovery of PGE as a by-product may be considered. Literature suggests that the Chinese may have already investigated this possibility (Cabri, and Laflamme, 1981). As such the Podiform chromite deposits should be strictly classed with the "other" miscellaneous deposits.

3)      Placer type

This type includes alluvial, eluvial and Alaskan derived type deposits. The alluvial and eluvial deposits are typically derived from weathered ultramafic rocks. The PGM typically occur as Pt-rich alloys in the form of loose grains or nuggets.

4)      Dunite pipes

Dunite pipes occur in the eastern and western sections of the Bushveld complex with grades up to 2000 g/t in some sections. The mineralogy of the pipes differs greatly from the Merensky and UG2 reefs in that the sulphides of the PGE are rare. Fifty percent of the PGM are present as Pt-Fe alloys; a further 30% of the PGM are present as sperrylite and geversite. These pipes were exploited in the early 1900's. The PGM were recovered using gravity recovery methods, with recoveries between 82% and 86%.

Ni-Cu DOMINANT ORES

The Ni–Cu dominant ores can be classified into the following types:

Noritic rocks associated with an astrobleme (meteoric impact). The only known example of this ore type is the Sudbury ore in Canada; Intrusive equivalents of flood basalt associated with intercontinental rifting. The most significant example of this ore type is the Noril'sk deposit in Russia. The Duluth complex in Minnesota is another example of this class of ore; Magmatic activity accompanying the early stages of formation of Precambrian greenstone belts which can be subdivided into two further classes: the Kola Peninsula, Lyn Lake, and Thompson and the Northern tip of the Ungava Peninsula in Canada; Tholeiitic intrusions, generally synchronous with orogenisis in Phanerozoic orogenic belts.

MISCELLANEOUS ORES

Porphyry Copper Ores: PGE are recovered from Cu refineries in the United States and Canada as a by-product. Copper-Molybdenum Deposits: Deposits in Armenia have measured up to 0.08 g/t Pd and 0.018 g/t Pt. Carbonatite: The Palabora carbonatite complex in South Africa produces Cu from a low-grade chalcopyrite-valleriite ore.

Black Shales: The base metal-bearing black shales from the Zechstein basin (Poland) contain PGE values ranging from 20 to 400 g/t. Some PGM have been identified but it is believed that the platinum forms organic compounds with kerogen.

Hydrothermal and Supergene Copper Ores: Pt and Pd-rich samples have been identified from the New Rambler mine in Wyoming.

Nickel-bearing Laterite Deposits: Ni laterites are formed by the chemical weathering of ultramafic and mafic rocks. The PGE hosted in the original rock are concentrated in the Ni laterite. Concentration ratios are reported to range from 0.7 to 7 times the values in the original host rock. An example of this type of deposit would be the Black Range Syerston Project in Central New South Wales, Australia.

Since the mid-1970's, the UG2 reef, in the Bushveld Igneous Complex, has been increasingly exploited for its PGE content. Until recently, the mining companies exploiting this reef were the same mining companies exploiting the Merensky reef, some 15 to 330 meters above the UG2 reef. In 1986, the Stillwater project heralded the first major primary PGE project in North America. The Lac des Iles mine (owned by North American Palladium Ltd.) followed the Stillwater success story in 1993 (Cole and Ferron, 2002-03). Canada has supplied PGE metals as a by-product of nickel and copper mining, primarily from the Sudbury and Thompson regions. Inco started production of PGE in 1908 when it opened a refinery in the U.K. to refine ores from the Sudbury basin.

## 21.2 PROCESSING TECHNIQUES RECOGNITION AND ANALYSIS

Processing techniques of PGMs include mineral processing to produce bulk concentrate (PGMs, Cu, Ni) and/or PGMs concentrate and sulphide concentrate (Cu, Ni), and metallurgical extraction to separate various PGMs and other metals.

### 21.2.1 MINERAL PROCESSING

#### 21.2.1.1 PGES DOMINANT ORES

The typical commercial method used for the recovery of PGE from primary ores (other than placer deposits) is flotation.

The "South African MF2" Flowsheet

The MF2 flowsheet (Figure 1) consists of a primary milling stage followed by primary flotation. The primary rougher tails are then re-ground and floated in a second stage, i.e. milling a rougher tail prior to scavenging. The primary rougher concentrate and the secondary rougher concentrate (scavenger concentrate) are cleaned in separate cleaning circuits with one to three stages of cleaning in each circuit. The cleaning circuits generally operated as a counter-current cleaning stages. The cleaner tails from the primary cleaner bank recycle to feed the primary rougher, while the cleaner tails from the secondary (scavenger) cleaner bank recycle to feed the secondary mill (Cole and Ferron, 2002-03).

Variations in the flowsheets are numerous and could include: The first rougher cells concentrate bypassing the cleaner circuit to report directly to final concentrate; Gravity concentration of rougher concentrate to recover liberated PGM that will bypass the smelter and report directly to the precious metal refinery; Flash or unit flotation incorporated into the primary milling circuit.
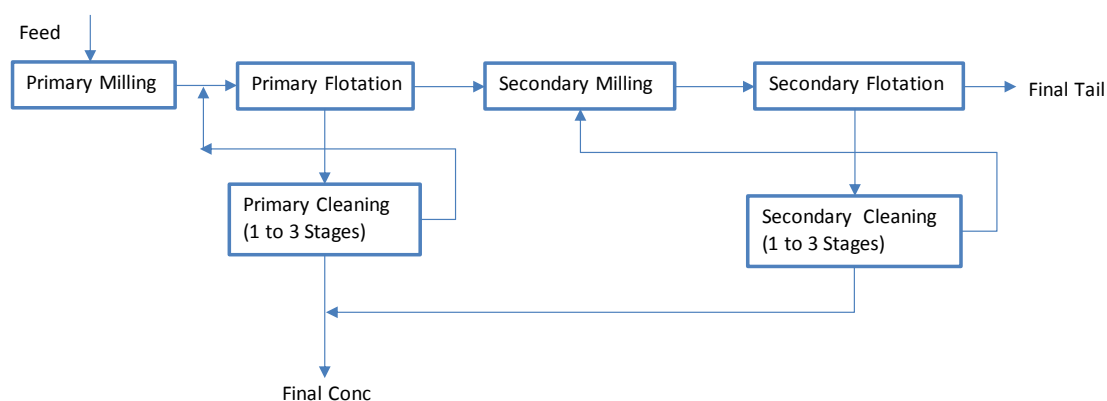


Figure 1. A Typical MF2 Flowsheet

The Northam Flowsheet, South Africa

The beneficiation flowsheet in the Northam Merensky concentrator (South Africa) is shown in Figure 2. In the ore the PGMs minerals are: braggite (Pt,Pd)S, cooperite, PtS, laurite RuS2, Pt–Fe alloy, sperrylite, PtAs2 and two tellurides (moncheite, PtTe2, kotulskite PdTe) etc. The base metal sulphides are pyrrhotite, pentlandite and chalcopyrite, and also some minor sulphides including cubanite, mackinawite and pyrite (Xiao and Laplante, 2004; Cole and Ferron, 2002; Brynard et al., 1976; Vermaak and Hendriks, 1976).

The Northam Merensky concentrator was designed to treat 270 t/h of run-of-mine (ROM) ore. A semi-autogenous grinding (SAG) mill operating in open circuit provides primary grinding. A ball mill operating in closed circuit provides secondary grinding. Flash flotation is utilized on the cyclone underflow. The flash flotation cell recovers over 60% of the PGE in the final concentrate. The cyclone overflow goes to flotation after conditioning. The primary flotation is undertaken in a single rougher/ scavenger flotation bank. The concentrate of the first cell in the rougher is collected as a part of the final concentrate. The other rougher concentrate is further processed with the cleaning circuit (no regrinding) that consists of three column cells operating in series. The cleaner concentrates are the main final concentrates. The cleaner tail is recycled back

to the head of the cleaner circuit. The scavenger concentrate can be routed to the head of the rougher or to the cleaner circuit. No grinding is performed on the scavenger concentrate (Cole and Ferron, 2002-03).

Flotation takes place at natural pH (7.5–9) with a xanthate collector such as isobutyl xanthate or normal propyl xanthate. To depress the talc, a depressant, such as Detrin or Carboxymethyl cellulose (CMC), is added to the rougher and cleaner stages (Xiao and Laplante, 2004).
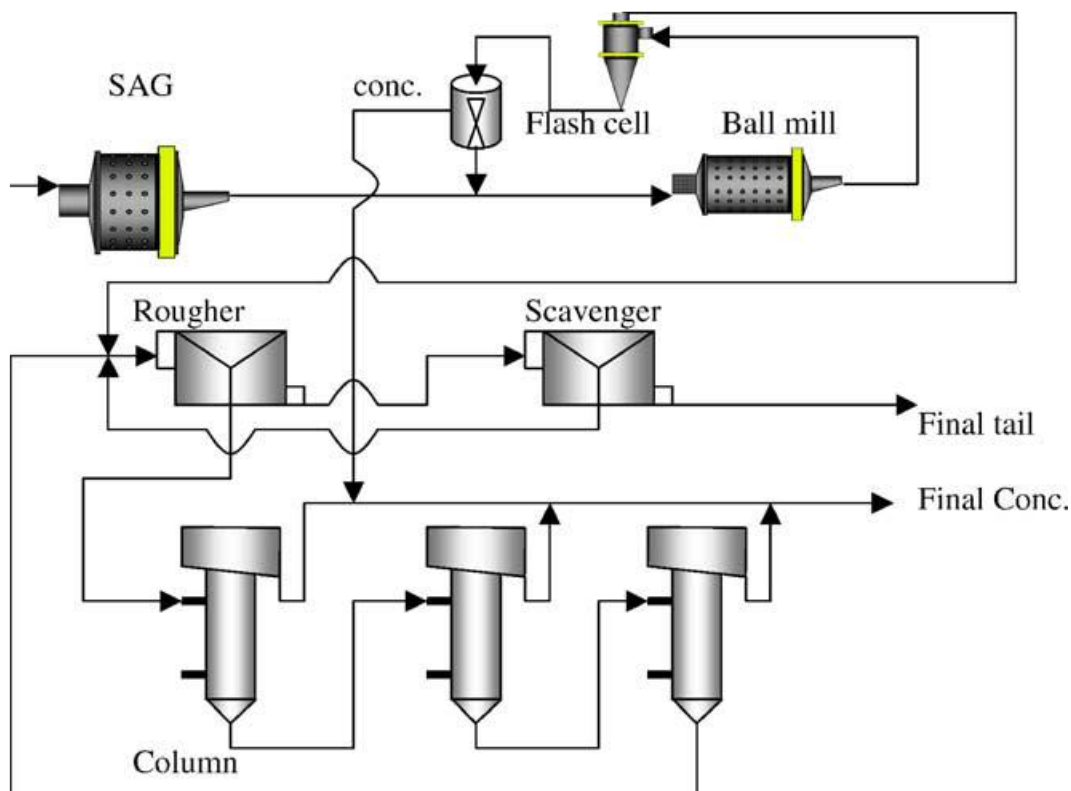


Fig.2 Beneficiation flowsheet at the Northam Merensky concentrator (Xiao and Laplante, 2004)

The Stillwater Flowsheet

The ore body at stillwater is referred to as the J-M reef and is nearly 30 miles in length. The PGEs mineralization is associated with disseminated base-metal sulphides minerals.

The dominant PGMs minerals are braggite, cooperite, moncheite, vysotskite and isoferroplatinum. Platinum occurs largely as discrete PGMs: 67% as sulphides minerals (braggite, cooperite); 25% as metal alloy (isoferroplatinum); and 8% as telluride (moncheite). Palladium largely occurs in solid solution in pentlandite; 15% of the palladium occurs in other sulphide minerals (vysotskite, braggite, cooperite) and 5% is associated with telluride minerals (moncheite). There are some rare PGMs, which include rustenbergite ($Pd_3Sn$), hollingworthite (RhAsS), etc. The grain size of the PGMs is variable, ranging from micron-size to grains with one side about 200 μm. Of the main PGMs, braggite and vysotskite are the coarsest grained; the Pt–Fe alloy is finer (Xiao and Laplante, 2004; Zientek et al., 2002).

The principal sulphide minerals are chalcopyrite ($CuFeS_2$), and pentlandite ($(Ni,Fe)_9S_8$). Most of the platinum minerals are associated with the copper sulphides and the palladium with the nickel sulphides (Thurman and Allen, 1994). The ore contains approximately 3.5 times more palladium than platinum. Small amount of gold

and rhodium along with the copper and nickel are also found. The ore contains less than 1% free silica, but significant amounts of MgO bearing minerals such as talc and serpentine.

The beneficiation flowsheet in the Stillwater Nye concentrator in Figure 3 (Thurman and Allen, 1994; Turk, 2001). A SAG mill/ball mill grinding circuit with hydrocyclones for classification is used to process ROM ore. Flash flotation is used to produce a final grade concentrate from the cyclone underflow. The cyclone overflow is fed to the rougher flotation. The rougher concentrate reports to the two stage cleaning flotation (1st and 2nd cleaner). The flotation columns are used at the 2nd cleaner and the final concentrate is obtained. The rougher tailings is fed to the middling flotation after grinding by a vertical stirred mill and then scavenger flotation to get the final tailings. A ball mill is used for the 1st cleaner tailings regrinding before the scavenger flotation.

The collectors used are potassium amyl xanthate, at a rate of 47 g/t and dithiophosphate (Cytec 3477), at a rate of 35 g/t. No frother is used as the ore is "naturally frothy" and 3477 is a mildly frothing collector. The original design did not use any 3477 but it was found to increase PGE recovery by 2-4% (Hodges, Clifford, 1998). The collectors are added to the flash flotation cell, the rougher conditioner and the middlings feed (Turk, 2001). Carboxylmethyl - cellulose (CMC) is used for talc control and is added at a total rate of 450 g/t (Hodges, Clifford, 1998). The CMC is added to the flash flotation cell, the rougher conditioner, the cleaner conditioner, the second cleaner feed and the middlings feed (Turk, 2001). Sodium hydrosulfide (NaHS) and sulfuric acid added as the modifiers.

The plant is reported to have a PGE recovery of 91% and is producing a concentrate containing 2000 g/t PGE. The plant has a capacity of 3000 tonnes ore per day (Dyas and Marcus, 1998).
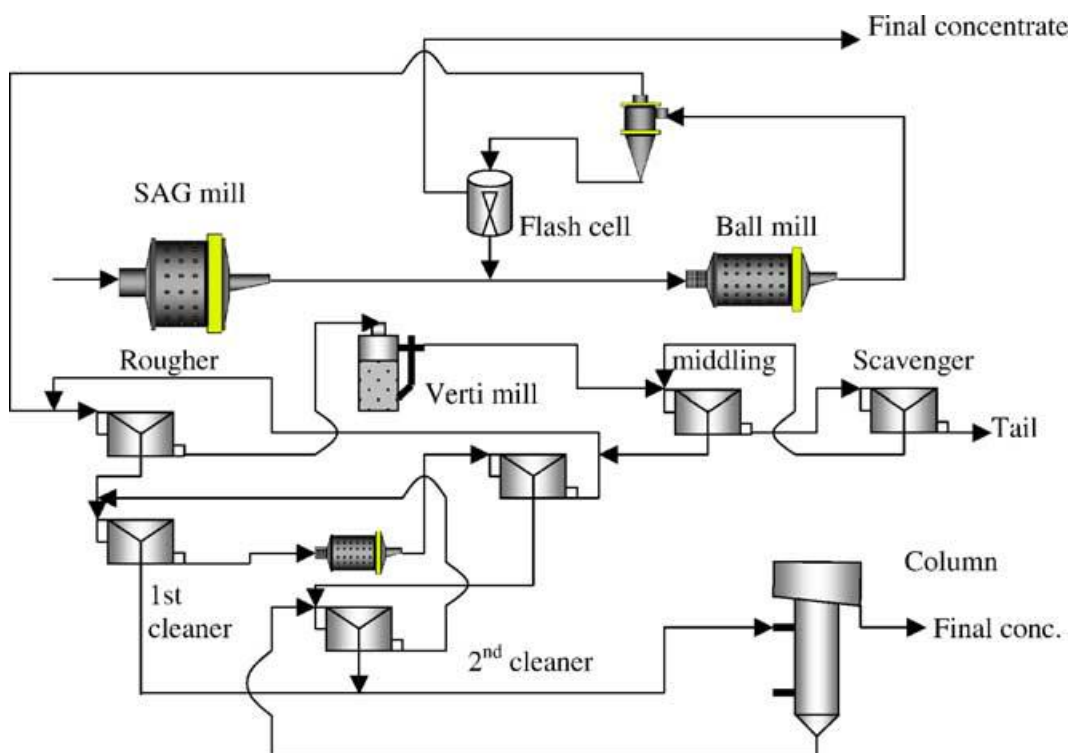


Fig. 3. The Stillwater flowsheet (Xiao and Laplante, 2004)

The Lac des Iles Flowsheet

Lac des Iles has recently commissioned a new concentrating facility as part of its expansion program to increase mill throughput from 2,400 to 15,000 tonnes per day (North American Palladium Ltd., 2001; Cole and Ferron, 2002-03).

The Lac des Iles ore in North American contains 2g/t palladium (and 0.3 g/t total platinum, gold and rhodium). Beginning commercial production in December 1993 the mine produces a concentrate assaying 250g/t palladium, at a recovery of roughly 75% (Martin and McKay, 2003) with open-pit mining. The major opaque minerals of the ore are pentlandite, pyrite, chalcopyrite and pyrrhotite. Galena, magnetite and sphalerite are common but minor minerals . The principal PGMs are braggite-series minerals (braggite, (Pt,Pd)S + vysotskite, PdS), kotulskite, PdTe, isomertiete, Pd11(As,Sb)4, merenskyite, PdTe2, sperrylite PtAs2, moncheite, PtTe2; minor PGMs include stillwaterite, Pd8As3, and palladoarsenide, Pd2As.

Host rock mineralogy is dominated by silicates. Feldspars, amphiboles and chlorite constitute more than 75% of the ore. Pyroxene, a major constituent of the South African PGM ores, is relatively uncommon at Lac des Iles. Much of it is altered to talc. The talc content in the Lac des Iles ore varies between 2 and 4 percent. Sulphides comprise about 0.6% of the Lac des Iles ore. In order of decreasing abundance, these include pyrite, chalcopyrite, pentlandite and pyrrhotite. PGM mineralogy consists, most predominantly, of palladium tellurides and arsenides, of which kotulskite and palladoarsenide are the most common minerals.

Beneficiation flowsheet is shown in Figure 4. One SAG mill feeds two ball mills at a rate of 15,000 tonnes per day. Two banks of roughers and scavengers perform the primary flotation. The rougher concentrate is reground and cleaned in a single stage column. The rougher cleaner tail joining the scavenger concentrate is reground in three vertical mills for further liberation due to the fine distribution of PGMs. The reground material is then cleaned in three stages, with the cleaners operating in a counter-current configuration. The scavenger cleaner tail reports to the final tail. Cleaner flotation uses two stages of cleaning with mechanical cells, and a third stage using flotation columns, the column tails being scavenged using a bank of mechanical cells (Cole and Ferron, 2002-03).
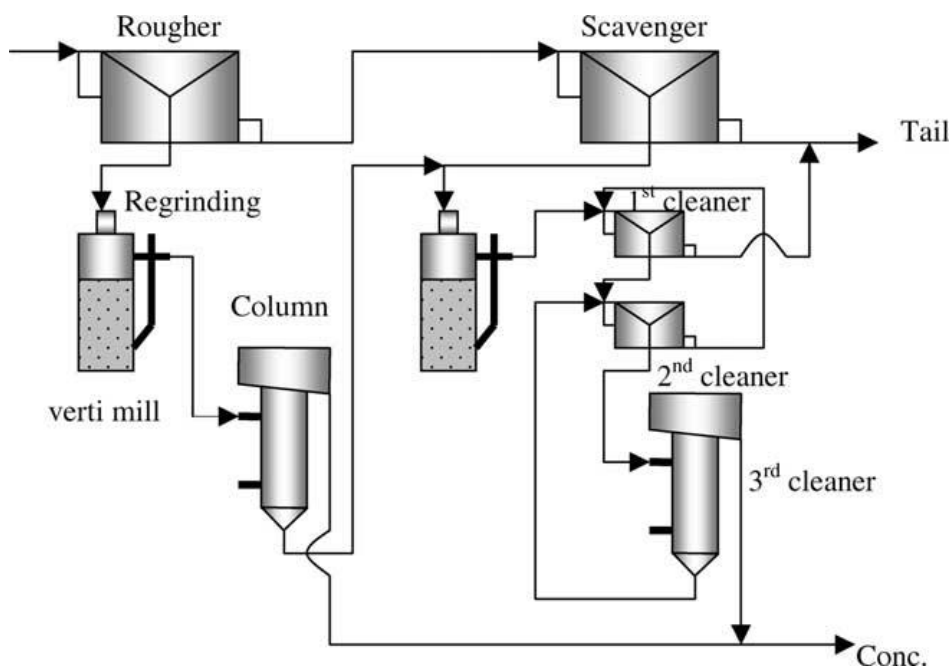


Fig. 4. The Lac des Iles flowsheet (Xiao and Laplante, 2004).

The flotation reagents consist of amyl xanthate collector, dithiophosphate promoter, MIBC frother and a polymeric talc depressant, usually a form of carboxy methyl cellulose (CMC) (Xiao and Laplante, 2004). Xanthates are added at rates varying from 30 g/t to 200 g/t. Dithiophosphates are added at rates varying from 10 g/t to 100 g/t. The collectors are generally added to the rougher feed and scavenger feed. CMC is used as a depressant and is generally added to the cleaning circuits. Various frothers are used by the various producers (Cole and Ferron, 2002-03).

In the South African deposits the concentration of PGMs is still less than 10 g/t physical and pyrometallurgical processes are applied to concentrate the PGMs (Figure 5) (Bernardis et. al., 2005; Seymore ET AL., 1998).

Ore (0.0005-0.0008% PGMs)
↓
Flotation
↓
Flotation Conc. (0.01-0.015% PGMs)
↓
Smelting → Slow cooling
↓
0.15% PGMs
↓
Magnetic separation → Cu-Ni sulfide Matte
↓
PGMs-rich Ni-Cu-Fe phase
↓
Dissolution → Ni-Cu-Fe solution
↓
60% PGMs Conc
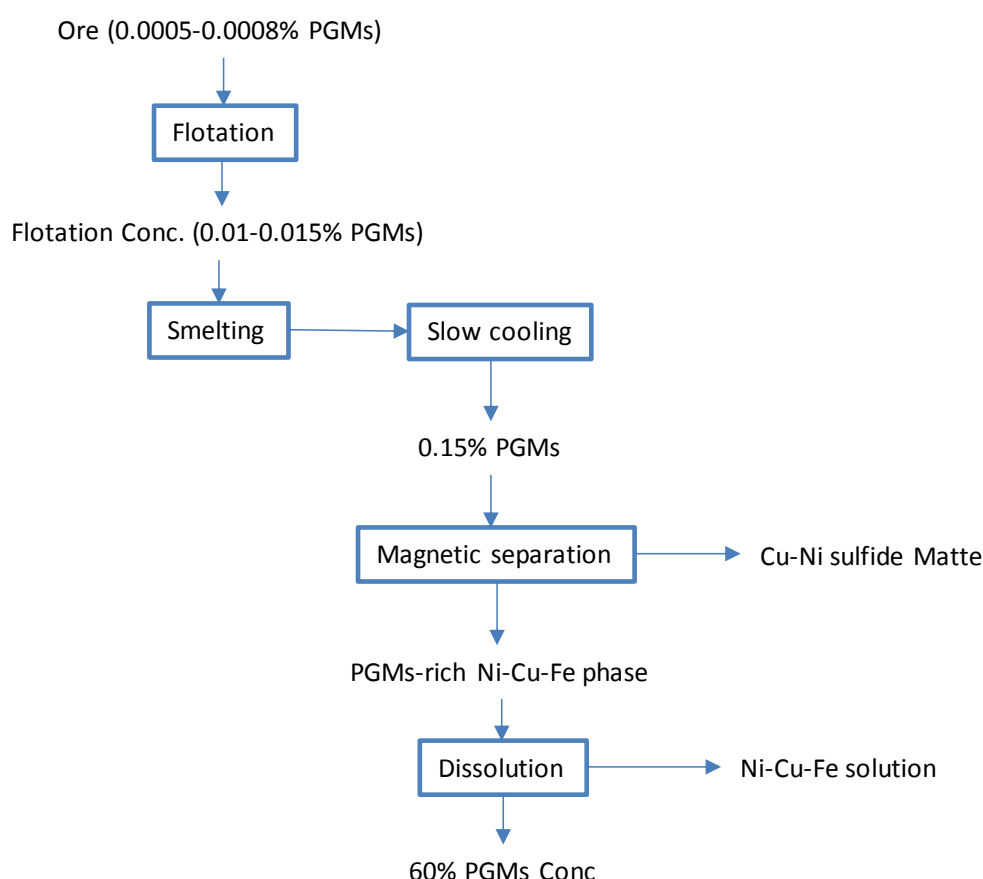
Fig.5. Concentration process for a PGMs sulfide ore in South Africa

## 21.2.1.2    NI–CU DOMINANT ORES

The Cu–Ni sulphide ores, mainly from the Sudbury area, Canada and the Noril'sk–Talnakh area, USSR, are very important sources for production of PGMs as a by-product (Cabri, L.J., 2002; Cabri, L.J., 1981a,b; Cabri, LJ., Laflamme, J.H.G., 1979; Xiao, Z., Laplante, A.R., 2003; Kozyrev, S.M.,2002).

The Sudbury ores

The principal sulphides are pyrrhotite, chalcopyrite, and pentlandite; several other minerals, such as cobaltite, pyrite, millerite, cubanite, galena, sphalerite, magnetite, etc., occur in minor and variable quantities in the ore. Michenerite, PdBiTe, is the principal palladium mineral and sperrylite, PtAs2, is by far the most common platinum mineral for many deposits (South Range and offset) (Cabri, 1981b). Moncheite, PtTe2, is the principal platinum mineral in deposits with essentially no sperrylite (Levack West). Froodite, PdBi2, insizwaite, PtBi2, and sudburyite, PdSb, are less common.

The PGEs in Sudbury ores is a by-product of smelting and refining Ni–Cu concentrates. Beneficiation concentration of PGEs is not available because PGEs in solid solution in other minerals such as arsenides, sulpharsenides, cobaltite and gersdorffite.  For the particular sample studied, from 1% to 4.5% Pt, 22.3% to 23.3% Pd and 31.2% to 41.2% Rh are present as solid solutions in cobaltite and gersdorffite (Cabri, 1981a ; Xiao and Laplante, 2004).

The Noril'sk–Talnakh ores

The Noril'sk-Talnakh deposits are situated north of the Arctic Circle in northern Siberia. Being different in mineralogy the three economic types of the Noril'sk–Talnakh PGEs–Cu–Ni sulphide ores are massive (rich) ore, disseminated ore occurring in host rock, and stringer-disseminated ore occurring in intrusive host rocks (Kozyrev et al., 2002 ; Xiao and Laplante, 2004).

At present nickel, copper and platinum-group elements are produced from six mines. Disseminated ore is being mined at an open cast operation on the Noril'sk I orebody, while the down dip extension is being mined underground in the Zapoljarni Mine. Four underground mines exploit the considerably larger Talnakh orebodies. These are the Oktyabrski, Taimirski, Komsomolski and Mayak Mines. In addition, the Gluboky and Skalesty Mines are presently being developed on the deeper parts of the orebody. Reserves of massive ores are estimated to last for another 50 years, and those of disseminated ores to last well beyond the twenty-first century at present production rates (Platinum Metals Rev., 1991, 35, (2), 96-100.).

The refineries at Noril'sk produce nickel, copper and cobalt metal. Platinum-group metals concentrate is shipped to a platinum refinery in Krasnojarsk. All raw materials for the refining of the base metals, such as coal and pure silica sands, are obtained in the immediate surrounding of Noril'sk. The slags are used for concrete back-fill of the underground workings, the cement being produced locally from limestone and gypsum deposits. Electricity is generated in two power stations, one at Talnakh and the other at Noril'sk from gas which is piped to these plants. The gasfields are about 150 km due west, in the sedimentary succession of the Yenisei trough (Platinum Metals Rev., 1991, 35, (2), 96-100.).

Massive ore:

The massive ores deposit refers to the Kharaelakh orebody in the Noril'sk–Talnakh area., which occurs at the base of layered intrusion and contain more than 70 vol.% sulphides. The orebody is subdivided into three groups, namely, pyrrhotite ore, cubanite ore, and chalcopyrite ore. Pyrrhotite ore includes pyrrhotite, chalcopyrite–pyrrhotite and cubanite– chalcopyrite–pyrrhotite varieties, which make up 85 vol.% of the Kharaelakh orebody (Xiao and Laplante, 2004).

Variability in the chemical composition of massive ore manifests itself in a gradual increase of PGEs content from 2.3–11.9 ppm up to 20.2–111.7 ppm (Kozyrev et al., 2002). The pyrrhotite ore has few PGMs in the -45 µm (75 wt.%) and 45–90 µm (25 wt.%) size fractions. These include isoferroplatinum (IFP), sperrylite, cooperite, rustenbergite, Kotulskite, merenskyite and native gold. The dominant PGMs is IFP, which constitutes 99 wt% of

the total PGMs assemblage ((Kozyrev et al., 2002). The major PGMs are amenable to flotation: sperrylite and cooperite are concentrated in copper concentrate (69% and 90% of the total PGMs, respectively) and in the nickel concentrate (29% and 8%); stibiopalladinite (74%) favours the nickel concentrate and the pyrrhotite concentrate hosts 70% of isoferroplatinum.

The selective flotation flowsheet for the massive ores is shown in Figure 6. In copper flotation, pine oil is used as a frothing agent and butyl dithiophosphate as a collector; in nickel flotation, T-80 serves as the frother, potassium butyl xanthate as the collector with sodium dimethyl dithiocarbamate as a depressant, NaHSO3 as a modifier and CaO is used to regulate alkalinity.
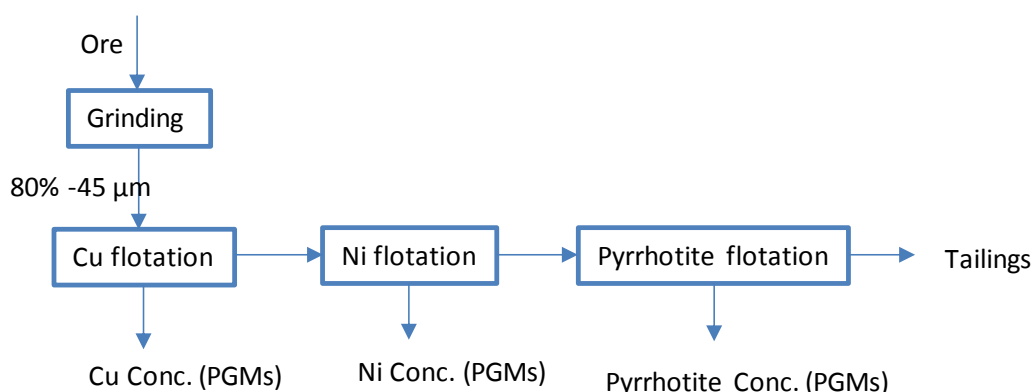


Fig. 6. Selective flotation flowsheet for massive ores (Xiao and Laplante, 2004)

Kozyrev et al. (2002) also characterized mineralogy of PGMs in the feed and concentrates of chalcopyrite–pyrrhotite and cubanite–chalcopyrite ores at laboratoryscale. It was found that chalcopyrite–pyrrhotite ore and process products contain 26 PGMs species. Palladium minerals are dominant (16 species), Pt constitutes nine minerals while Rh occurs in only one species. Most of the PGMs occur in the )45 lm size fraction (67–91 wt.%) of the primary ore as well as of the process products. The 45–90 lm size fraction of the nickel concentrate contains 66 wt.% of the PGMs. PGMs have not been detected in the tailings.

Kozyrev et al. (2002) also reported that the cubanite– chalcopyrite–pyrrhotite ore and concentrates contain the most PGMs in the 20–45 lm size fraction (42–84 wt.%). Twenty-nine PGMs have been identified and these include 18 Pd species and 11 Pt species. The major PGMs in the flotation feed are cooperate (28 wt.%), atokite–rustenburgite (24 wt.%) and sperrylite (20 wt.%); copper concentrate has sperrylite (42%), cooperite (24 wt.%) and isoferroplatinum (14 wt.%); nickel concentrate contains cooperite (36 wt.%), sperrylite (15 wt.%), atokite–rustenburgite (23 wt.%) and sobolevskite (11 wt.%); the pyrrhotite concentrate has isoferroplatinum (41 wt.%) and cooperite (20 wt.%) while the tailings have atokite–rustenburgite (54 wt.%) and sperrylite (17 wt.%). Most of the major PGMs grains in the concentrate are liberated while some occur as complex intergrowths with each other, with sulphides and with silicates.

Disseminated ore:

Three varieties of disseminated ores have been distinguished: (1) pyrrhotite ore, the most abundant, (2) cubanite, and (3) chalcopyrite ores, which are less abundant. The major sulphide minerals in pyrrhotite ore are the pyrrhotite-group minerals, chalcopyrite, pentlandite, with some minor and accessory minerals. Major sulphide minerals in the cubanite ore are cubanite, chalcopyrite, pyrrhotite and pentlandite; minor sulphides

includes mackinawite, sphalerite, galena etc. The chalcopyrite ore includes the following major sulphides: chalcopyrite-group minerals, pentlandite, pyrrhotitegroup minerals and cubanite. Some minor sulphide minerals also appear in this type of ore (Xiao and Laplante, 2004).

Gravity–flotation techniques have been developed to increase the PGMs recovery, such as recovering PGMs from concentrates, as well as scavenging of the Noril'sk mill tailing using gravity concentration methods (Kozyrev et al., 2002). The Knelson concentrator has been used by Kozyrev et al. (2002) to study the PGMs distribution in the Noril'sk mill gravity products.

Mineralogy: Kozyrev et al. (2002) reported that 26 PGMs species plus alloys of gold and silver have been found in the gravity concentrates of Knelson 12 in. concentrator and include 19 Pd minerals, 6 Pt minerals and a Rh minerals. Most of PGMs recovered is in minus 45 μm and 45–75 μm size fractions. In the latter size fraction, the most abundant (80 wt.%) of platinum minerals are isoferroplatinum, rustenbergite, and sperrylite; in the former, Pd species of the atokite–rustenburgite series dominate, with a twofold decrease of Pt–Fe alloy. Most PGMs grains and intergrowths (90%) in concentrates are liberated while the rest (10%) are attached to sulphides.

Recovery method (Figure 7): The fineness of grinding is about 55% -74 μm. Gravity concentration uses Knelson concentrators of various capacities to separate the noble-metal minerals. Bulk flotation produces a concentrate that undergoes further grinding to further liberate the minerals. Cleaning stages are used to produce higher-grade concentrates, which are processed further to produce copper and nickel concentrates. For flotation, potassium butyl xanthate and sodium butyl dithiophosphate serve as collectors, T-80 as a frother and CaO as a depressant.
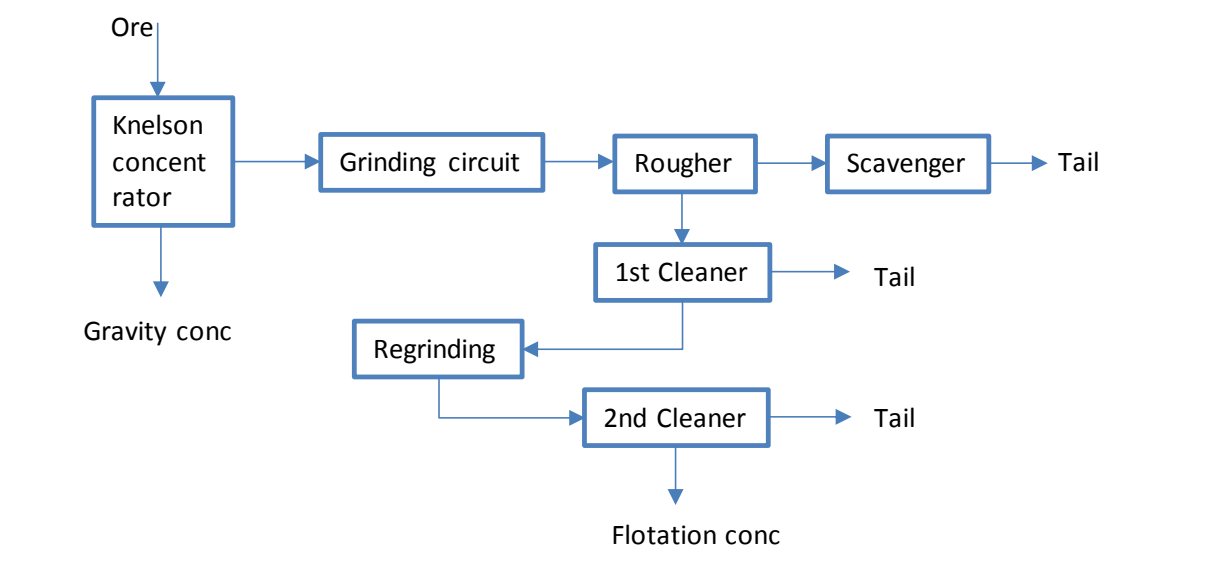


Fig. 7. Recovery flowsheet for disseminated ore (Xiao and Laplante, 2004)

## 21.2.2 METALLURGICAL EXTRACTION

As shown in Table 1 the PGE concentrates are too low-grade to be refined directly, and will need to undergo an enrichment step prior to refining. On the other hand, their value is so high that the enrichment step has to occur with minimum losses. The enrichment step for primary and secondary sources of PGE concentrates (high

and low grades) will be considered first, followed by the refining step before discussing new developments (Cole and Ferron, 2002-03).

Table 1. Grades and Values of High Grade PGE and Typical Base Metal Concentrates

| CONCENTRATE TYPE | GRADE | VALUE * (US$/TONNE) |
|---|---|---|
| Copper | 20-30% Cu | 370-560 |
| Zinc | 50-60% Zn | 460-555 |
| Lead | 60-70% Pb | 290-340 |
| Nickel | 5-12% Ni | 330-790 |
| PGE | 0.02-0.2% PGE | 2,330-23,330 |
| Cu: 85 ç/lb; Zn: 42 ç/lb; Pb: 22 ç/lb; Ni: 3 $/lb; PGE: 350 $/oz | | |

## 21.2.2.1    ENRICHMENT OF PGE CONCENTRATES

**High Grade Concentrates**

Typical concentrate grades will range from 200 g/t PGE to over 2,000g/t. The enrichment is usually a two-step process consisting in a pyrometallurgical step followed by a hydrometallurgical step (Figure 8) (Cole and Ferron, 2002-03).
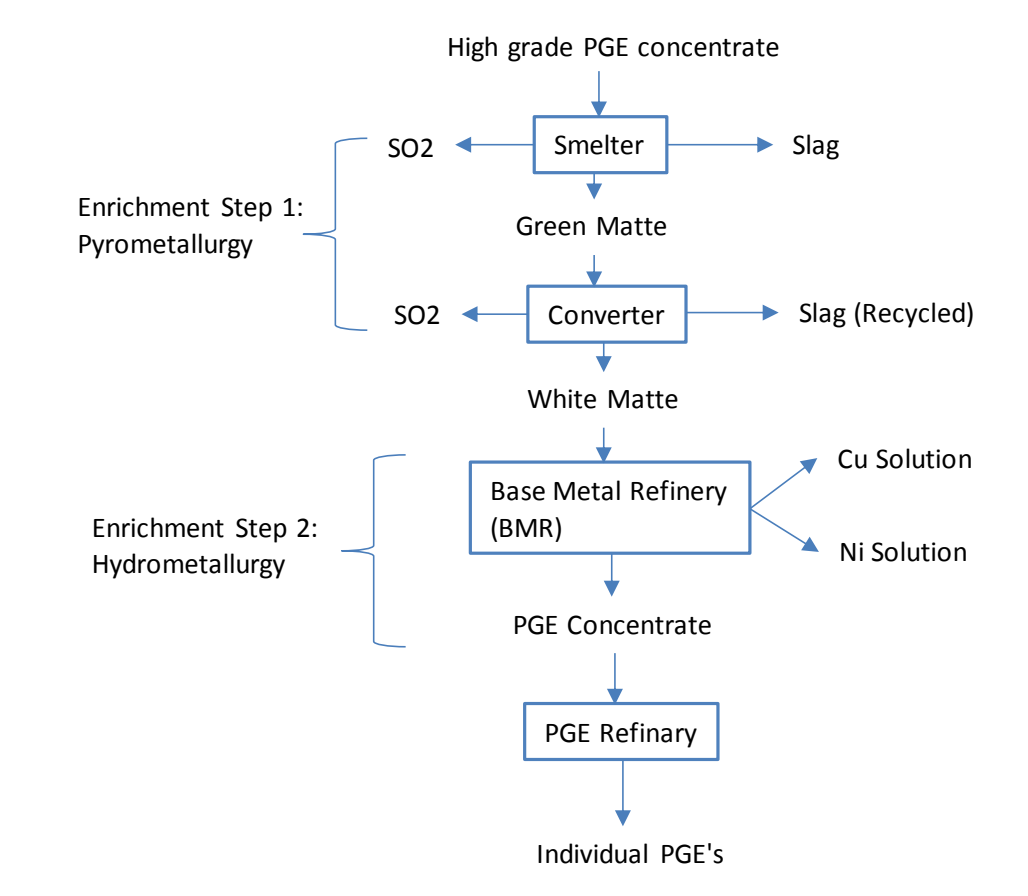


Fig.8 The two-step enrichment process

*Pyrometallurgical Enrichment :*

Flotation concentrates generally need to conform to many specifications to render them ideal for smelting. Parameters that tend to be important for concentrates generated from primary PGE producers include:

• Sulphur content (if needed, sulphide rich ores are added to the smelting furnace to collect the PGE)

• MgO content (typically 15-20%). Excess MgO is deleterious;

• $Cr_2O_3$ content (typically 0.4 - 2.8%). Excess $Cr_2O_3$ is deleterious; and

• Deleterious elements for smelting, e.g. arsenic and bismuth

Limitations of the conventional smelting and converting processes (Jones, 1999) include:

• $SO_2$ emissions from the converting process are a continuing environmental concern. Intermittent operation of the converters makes handling of the off-gas in a sulphuric acid plant difficult.

• If ores with low sulphide contents are processed, additional base metal concentrates need to be purchased to provide sufficient matte to allow for effective coalescence of the droplets and collection of valuable metals.

To meet $SO_2$ dispersion criteria in some parts of the world, smelters have to be shut down during certain climactic periods (low wind velocities, temperature inversions, etc).

• Discontinuous operation of converters is not conducive to stable plant operations.

The flotation concentrate composition must be suitable for smelting. Its rock mineral content should produce a fluid slag at the desired temperature. At the same time, it must contain enough sulphides to form a reasonable quantity of matte. To compensate for minor problems with chemical composition, various fluxes are added. Typically, the main addition is burnt lime or limestone but other materials such as carbonaceous reductants, sulphides, oxides or silicates are used as necessary. Table 2 summarises typical concentrate analysis from South African smelting operations (Jones, 1999). Note the higher $Cr_2O_3$ and PGE contents for the UG2 ores. It is also interesting to note the low Cu and Ni values in all of the concentrates.

The concentrates are smelted in electric furnaces. Large units with three to six electrodes in line are used for smelting. Smaller circular furnaces are used to smelt unblended chromite concentrate. Higher temperatures are required to melt chromite concentrates (such as the UG2 concentrates) owing to higher contents of chromium and magnesium oxides. More turbulent smelting conditions are also preferred to avoid build-up of chrome spinel in the furnace hearth. Typically, furnaces are run at about 1350°C, the UG2 furnaces can run at temperatures of up to 1600°C. On melting, the concentrate separates into two layers. The upper layer is a silicate/oxide iron-rich slag, which is tapped off and then either discarded or returned to the concentrator to recover any remaining PGE. The lower layer is an iron sulphide-rich green matte which is sent for converting. The sulphide minerals form the matte, prills of molten matte coalesces in the slag and then settle out under the influence of gravity (slag S.G. ~ 2.7-3.3, matte S.G ~ 4.8-5.3). The rate of settling is controlled by the viscosity of the slag which in turn can be controlled by the addition of fluxing agents such as limestone. The matte and slag are often tapped at opposite ends of the furnace. The energy requirement for smelting varies from 600-1000 kWh per tonne of concentrate depending on the nature and grade of the material being treated. The power flux in the furnaces varies between 90 and 235 kW/m2. The higher power fluxes are required for the UG2 ores.

The furnaces run with a slag to matte production ratio of between 3.5-9.0. Tables 3 and 4 show typical furnace matte and furnace slag analysis from the various South African producers.

The furnace matte is further processed by converting. i.e. blowing of air into the molten charge, over a period of a few hours, to oxidise and remove the iron and its associated sulphur. The oxidation reactions are sufficiently exothermic to maintain a temperature of about 1250°C. The temperature in the converter is controlled by adding cold feed or revert material to the charge. Fluxing agents (mainly silica sand) are added to form an iron-rich slag that is skimmed off and returned to the furnaces. The converter matte is granulated or slow-cooled. If the matte is slow cooled the PGE concentrate on the grain boundaries and tend to form ferromagnetic species that can be recovered by magnetic separation. These ferromagnetic phases are sent directly to the precious metal refinery (Jones, 1999; Chamber of Mines of South Africa, 2001). The converter slag requires further treatment as the vigorous turbulent conditions in the converter cause entrainment of the matte in the slag and oxidising conditions cause some base metals to dissolve in the slag in oxide form. The converter slag is usually returned to the smelting furnace, however, in some cases it is treated in a separate slag-cleaning furnace. Tables 5 and 6 show typical converter matte and converter slag analysis from the various South African producers.

As an example of state-of-the-art smelter, Anglo Platinum is presently installing a new smelter complex in Pietersburg, South Africa. The new furnace has been designed by Hatch and is a single, six-in-line-electrode, furnace, of 68 MW nominal operating power installed, capable of smelting 600,000 tonnes per annum of concentrate. Latest advances in furnace technology (waffle cooler) and design will allow it to treat concentrates with elevated levels of chromite (UG-2) (Cole and Ferron, 2002-03).

Slag will be tapped continuously, granulated and transported to a slag dump. The green matte is tapped, cast, cooled, crushed to minus 2 mm to suit the new converter at Waterval. This new converter, an Ausmelt reactor, will produce white matte in two stages. The converter slag containing too high PGE values has to be recycled to the process. Before, when treating low chromite concentrates, the slag could be recycled to the furnace; presently, for high chromite concentrates, the slag is treated by milling and flotation, but a slag cleaning furnace (a 30 MVA circular, 3-electrode furnace) is currently under construction and will be operational in the fourth quarter of 2002 (Cole and Ferron, 2002-03)

Power intensity of modern furnaces has significantly increased over the last 35 years, which in turn puts much pressure on the type and quality of refractories and on better means of removing heat from the system (waffle cooler) (Wasmund, Francki, 2001).

*Hydrometallurgical Enrichment - The Base Metals Refinery :*

The hydrometallurgical enrichment step consists of a reverse leaching operation whereby most of the accompanying minerals (copper, nickel, cobalt and iron sulphides) are dissolved to leave behind an upgraded PGE concentrate for the PGE refinery. For the high-grade PGE refineries, there are essentially two processes used commercially, the Outokumpu process and the Sherritt Gordon process. The chemistry underlying both processes is the same. The only PGE base metal refinery using the Outokumpu process was that of Hartley Platinum, in Zimbabwe. That refinery is no longer in operation. All of the other PGM Base Metal refineries in the Western World use the Sherritt Gordon process. A typical example is the process used at the Rustenburg Base Metal Refiners, in South Africa, as presented in Figure 9 (Cole and Ferron, 2002-03).

The production data for the main high PGE matte refineries in the Western world, collected from various sources, are summarised in Table 2.
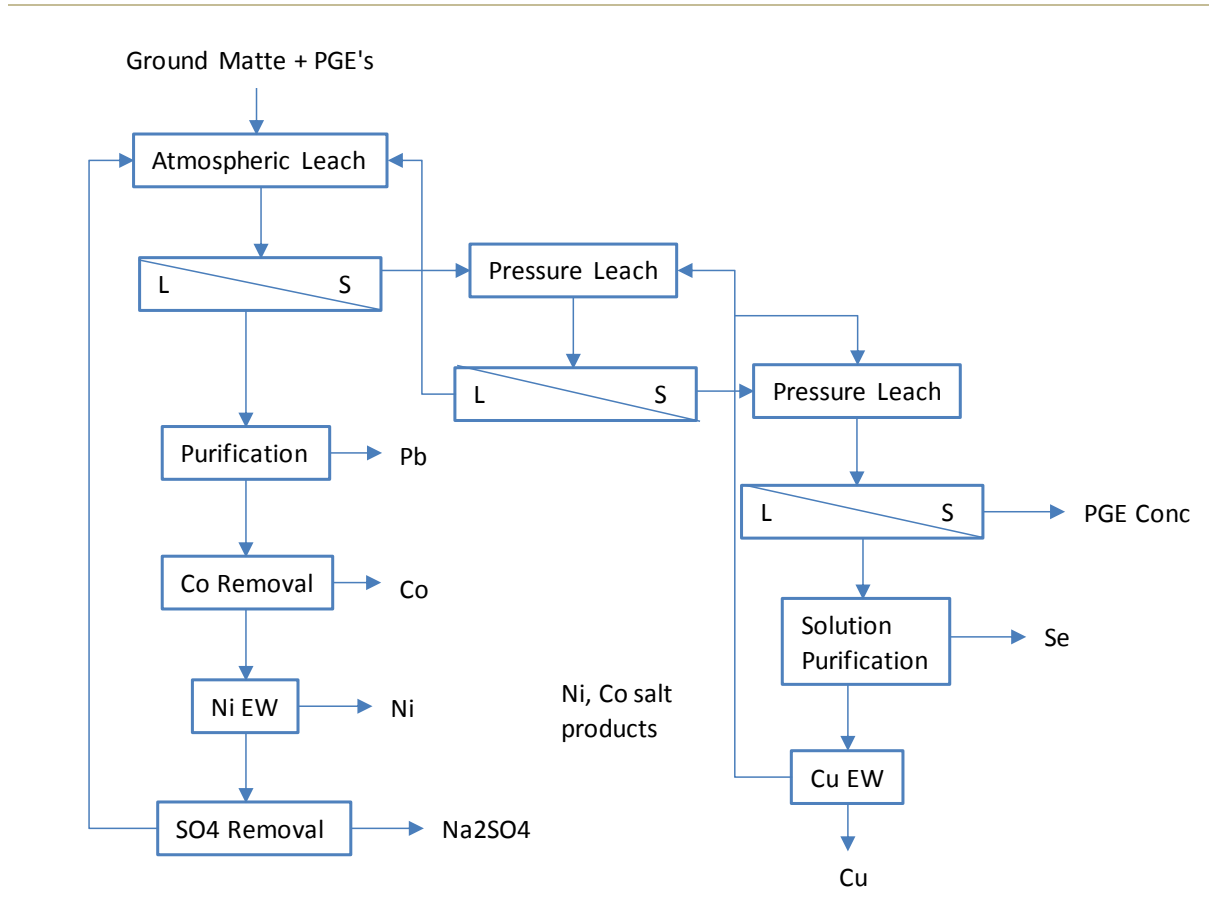
Figure 9. Simplification of the Sherritt process

Table 2. Summarises production data for the main high PGE matte refineries in the Western world, collected from various sources.

| PGE Matte Refinery | Matte Composition | | | | | Base Metal Leach Process | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Ni % | Cu % | Fe % | S % | PGE % | Type | Oxidant | Temp (°C) | Pressure (kPa) |
| Stillwater | 42.5 | 28.1 | 3.1 | 22.6 | 2.1 | S | O2 | Amb-135 | Atm-1000 |
| Hartley* | 44 | 33 | 1.0 | 21 | 0.15 | O | O2 | 85-150 | Atm-unknown |
| Impala | 50 | 28 | 1.0 | 20 | 0.15-0.2 | S | Air | 135 | 900 |
| Rustenburg | 47 | 22 | 3.0 | 21 | 0.15-0.2 | S | Air | 135 | 1000 |
| Western Palts | 48 | 28 | 0.5-1 | 21 | 0.15-0.2 | S | O2 | 85-165 | At-1100 |
| S=Shrritt Process; O=Outokumpu Process; Amb=ambient; Atm=atmospheric *Not operating at present | | | | | | | | | |

**Lower PGE Grade Concentrates**

As opposed to the PGE producers discussed previously, the PGE, although significant contributors to the overall economics of these operations, are nevertheless a by-product of nickel (mostly), copper and cobalt. The process is, therefore, designed around the major metal (nickel), while also maximising PGE recovery (Cole and Ferron, 2002-03).

Inco

As shown in Figure 10 starting from a low PGE grade (1 g/t PGE) in the mixed ore, Inco produces refined nickel and copper and by-product precious metal concentrates, as anode slimes and carbonyl process residues. The residue from the carbonyl process assays 55-60% Cu, 6-10% Ni, 4-8% Co, 4-9% Fe, 13-19% S, 600-900 g/t (Au + PGE) and 750 - 1350 g/t Ag. It is treated in a two-stage pressure leaching process to dissolve first the nickel and the cobalt, and then the copper + selenium + tellurium. PGE concentrate from the nickel circuit contains 60-80% (PGE + Au), plus some silver and a variety of base metals such as tellurium, antimony, tin, lead, bismuth, copper, nickel and iron. Concentrate from the copper circuit is largely palladium and platinum, with some rhodium, and generally much less base metals that the concentrate from the nickel anode slimes. These concentrates are refined in the Inco's Acton refinery in the UK.
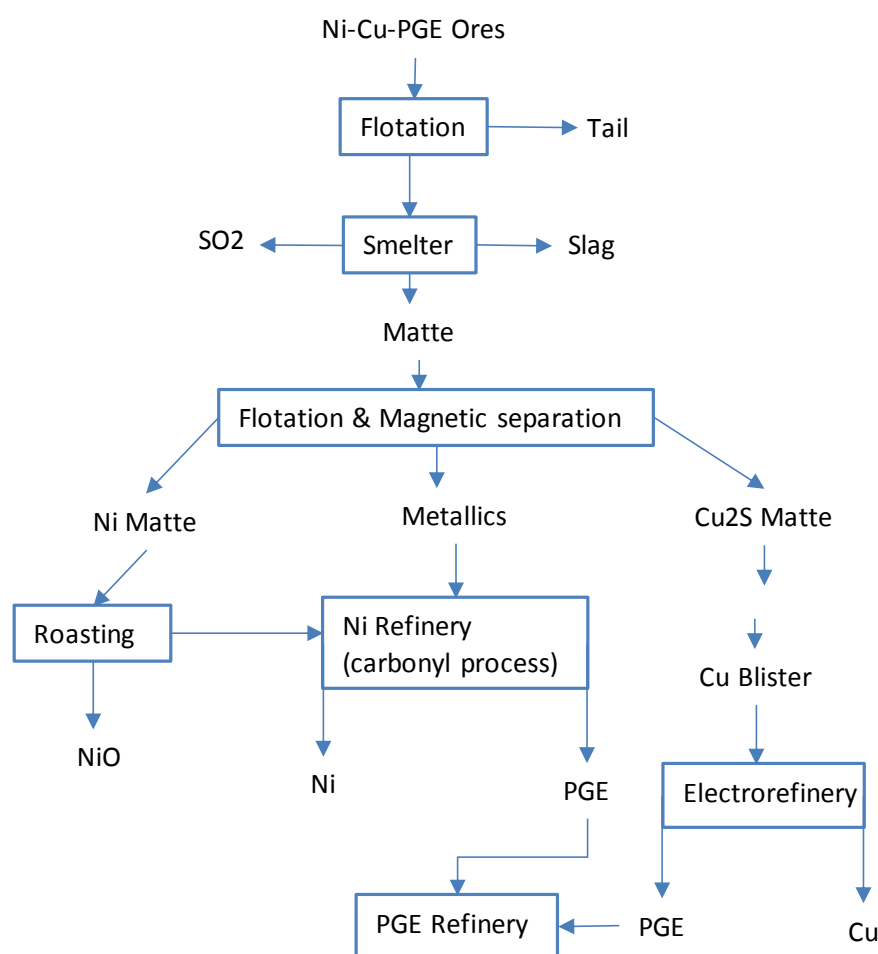


Fig.10 Recovery of PGE's during Inco's Treatment of Sudbury Ores

Falconbridge

Falconbridge in Sudbury treats ores similar to Inco's but the approach to recover base metals and the PGE is completely different. The nickel and the cobalt are fully recovered to pure metals from a chloride system; the copper is roasted to sulphates and recovered conventionally from sulphate solutions. The PGE are concentrated in the sulphuric acid leach residue. The residue is reduced to metal using hydrogen, and leached with chlorine under controlled redox potential to minimise the dissolution of PGE's. The solid residue is the primary PGE concentrate; it is smelted to matte in an electric furnace; the matte is granulated and leached with HCl/Cl2 to obtain the final PGE product.

## 21.2.2.2    PGM SEPARATION AND PURIFICATION

**Classical precipitation methods**

Up until the mid 1970s the separation of the PGMs was achieved largely using a series of precipitation reactions. The outline presented in Figure 11 is largely based on one used by International Nickel Co. (INCO). Relatively poor selectivity was obtained for many of the precipitation steps which is both due to the presence of interfering precipitation reactions and the entrainment of liquor associated with solid–liquid separations. The numerous unit operations and recycle streams have lead to lengthy refining times and made the refining process labour intensive (Bernardis et. al., 2005).
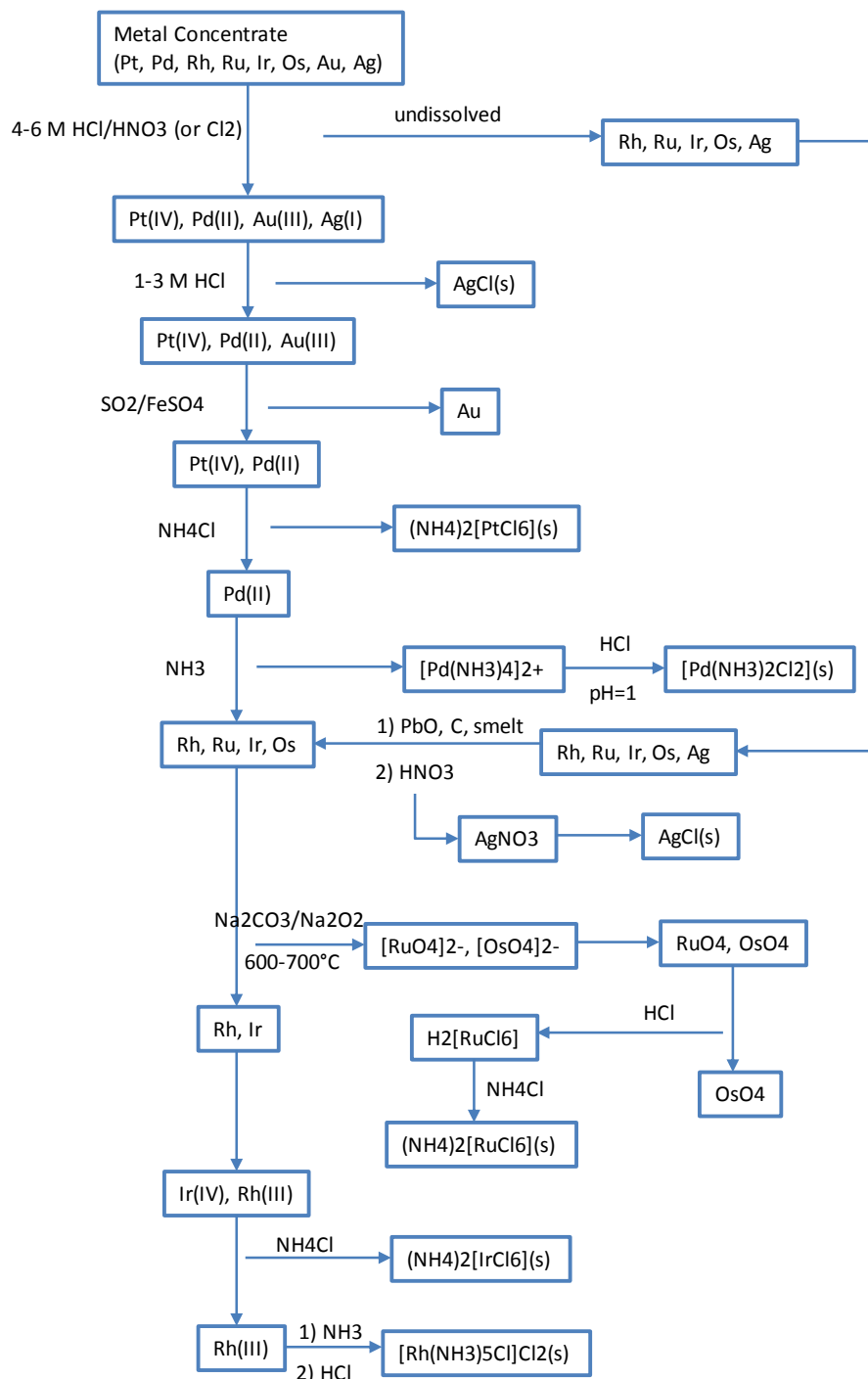
Fig.11 Classical refining method for the separation of the PGM

**Solvent extraction methods**

A number of solvent extractants were introduced in commercial PGM refineries in the mid 1970s and are still used today. Essentially three different types of extractants have found use, which are distinguished by their mechanism of extraction. These are listed in Table 3 along with examples of extraction systems (Bernardis et. al., 2005).

Table 3  Solvent extractions used in PGM refining

| Mechanism | | Solvents | Metal(s) selectively extracted under process conditions |
|---|---|---|---|
| Complex formation | | Dialkyl sulfides, hydroxyoximes | Pd(II) |
| Anion exchange | Strong base | Tri-n-octylamine | $[MCl_6]^{2-}$ |
| | Weak base | Dibutyl carbitol, isodecanol, methyl-iso-butyl ketone | $[AuCl_4]^-$ |
| | | Tri-n-butyl phosphate | $[MCl_6]^{2-}$ |

Solvent extraction offers a number of advantages over the classical precipitation methods: (1) higher selectivity is obtained with solvent extraction, (2) with the use of scrubbing techniques high metal purity is obtained and (3) more complete removal of metals is also possible through the use of multi-stage extraction. These have reduced the need for excessive recycling, shortened the refining times significantly and lowered production costs. The scrub liquors however represent recycle streams which need to be reprocessed, should they contain significant quantities of PGMs (Bernardis et. al., 2005).

The solvent extraction process comprises three basic steps: (1) an extraction step, to extract selectively a given metal; (2) a scrubbing step, to remove co-extracted metals and (3) a stripping step, to remove the extracted metal from the organic phase. These are represented in Figure 12, which also shows how streams can be recycled. With the advent of solvent extraction, methods were also developed to achieve complete dissolution of the PGM from the concentrate which also greatly simplified refining schemes. The flowchart presented in Figure 13 is based on a refining method used by Matthey Rustenburg Refiners on South African ores (Renner, 1992).
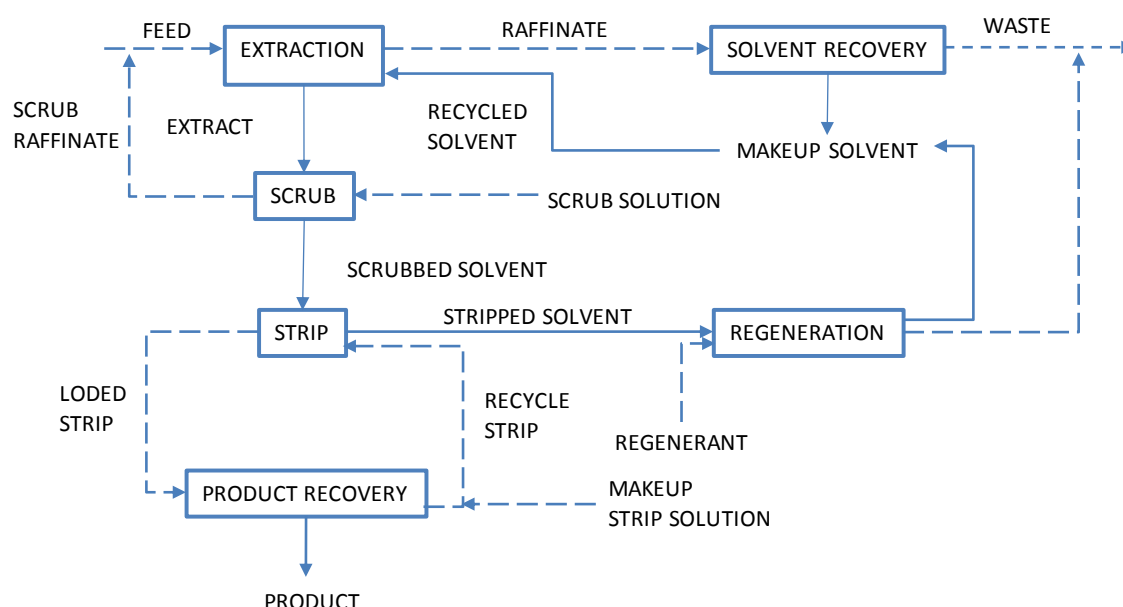
Fig.12 The general process of solvent extraction (Lloyd, 2004)
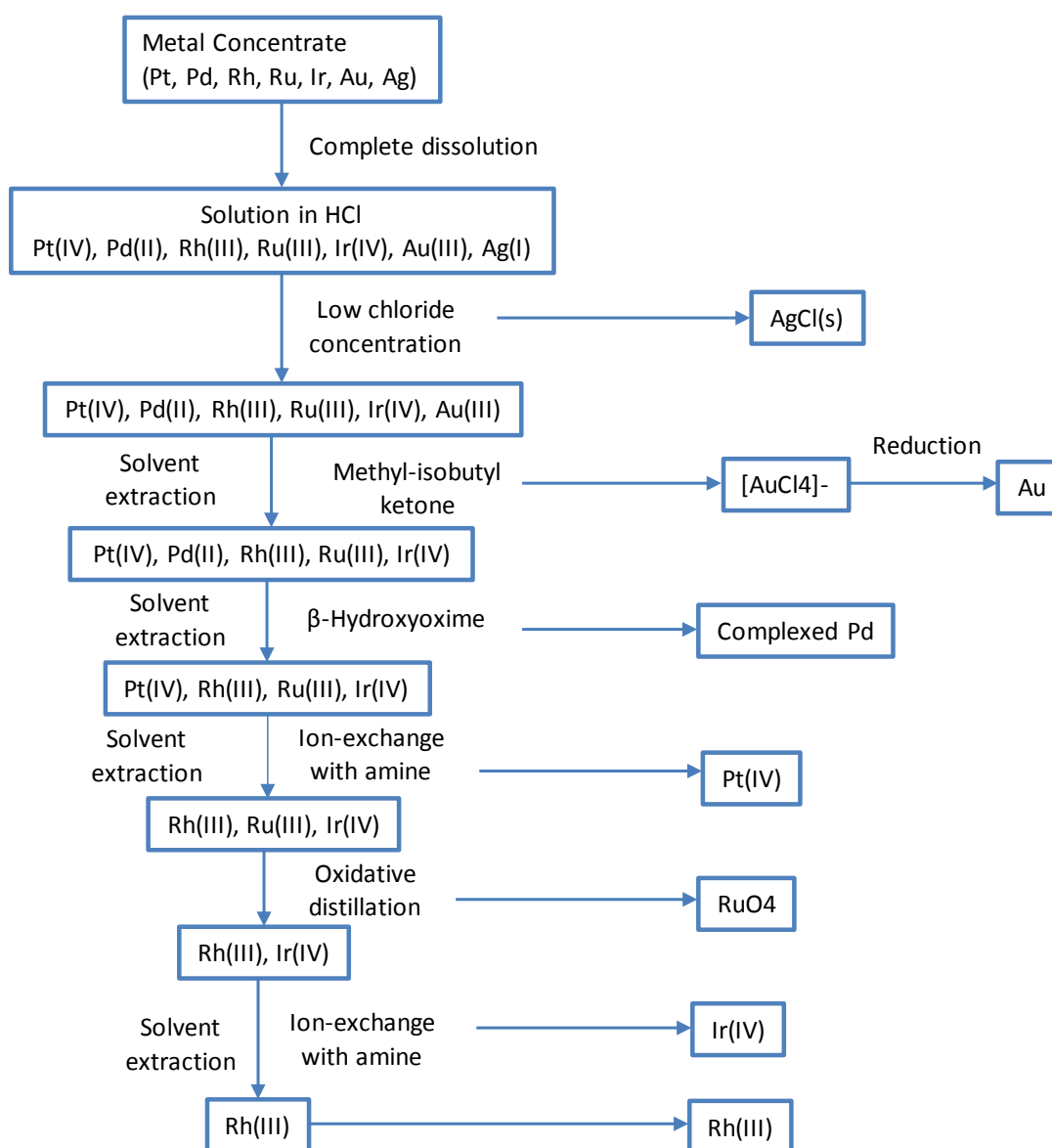


Fig.13 Modern refining method incorporating solvent extraction/ion-exchange

Southern Africa was the site of one of the first large solvent-extraction (SX) plants built, following smaller plants in the North American uranium industry and the Ranchers and Bagdad copper plants in Arizona. The copper Tailings Leach Plant at Nchanga, Zambia, was commissioned in 1973 with a capacity of 2800 m$^3$/h. This was the largest SX plant in the world for more than a decade and is still operational today. South Africa witnessed the first commercial implementation of SX for the refining of the platinum-group metals. More recently, southern Africa has seen the implementation of SX for other base metals, precious metals, and specialty metals. These include the bworld firstsQ of primary production of zinc using SX by Skorpion Zinc in Namibia, and the large-scale refining of gold by SX at Harmony Gold, South Africa. Several other flowsheets that use SX technology are

currently under commissioning, development, or feasibility study for implementation in this part of the world, including those for cobalt, nickel, vanadium, tantalum, and niobium (Kathryn C. Solea et al., 2005).

A review of SX operations in the African subcontinent is presented, with particular attention paid to advances since the turn of the millennium. Several interesting projects under development are also discussed, along with some innovative concepts in flowsheet chemistry that should soon reach commercial application (Kathryn C. Solea et al., 2005).

Liquid–liquid extraction/separation of platinum(IV) and rhodium(III) from acidic chloride solutions was carried out using tri-iso-octylamine (Alamine 308) as an extractant diluted in kerosene (Jin-Young Lee et al., 2009). The percentage extraction of platinum(IV) and rhodium(III) increased with increase in acid concentration up to 8 mol L−1. However, at 10molL−1 HCl concentration, the extraction behavior was reversed, indicating the solvation type mechanism during extraction. The quantitative extraction of ∼98% platinum(IV) and 36% rhodium(III) was achieved with 0.01 mol L−1 Alamine 308. The highest separation factor (S.F. = 184.7) of platinum(IV) and rhodium(III) was achieved with 0.01 mol L−1 Alamine 308 at 1.0 mol L−1 of hydrochloric acid concentration. Alkaline metal salts like sodium chloride, sodium nitrate, sodium thiocyanate, lithium chloride, lithium nitrate, potassium chloride and potassium thiocyanate used for the salting-out effect. LiCl proved as best salt for the extraction of platinum(IV). Temperature effect demonstrates that the extraction process is exothermic. Hydrochloric acid and thiourea mixture proved to be better stripping reagents when compared with other mineral acids and bases.

The extraction of Rh chlorocomplexes with trioctylamine (TOA) or with Aliquat 336 (diluted with toluene) and its subsequent separation from Pd and Pt was studied (G. Levitin and G. Schmuckler, 2003). Species distribution calculations showed that the predominant species of 22 Rh–Cl present in 1 M HCl is Rh(H O)Cl . Spectrophotometric measurements of Rh–chloride in the organic phase showed 2 5 22 32 that Rh(H O)Cl is being extracted and slowly converted into a dimer, Rh Cl . Stripping is carried out with concentrated 2 5 2 9 HCl. It is difficult to separate Rh chlorides from Pd and Pt by solvent extraction, and a gel-chromatographic method is therefore proposed in order to solve this problem.

The solvent extraction and separation performances of Pd(II) and Pt(IV) from hydrochloric acid solutions were investigated using dibutyl sulfoxide (DBSO) diluted in kerosene (Lu Pan and Zu-de Zhang, 2009). Pd(II) was strongly extracted by a lower concentration DBSO in a lower concentration hydrochloric acid solution while the reverse was obtained for Pt(IV) extraction. Based on independent extraction and separation experiments of Pd(II) and Pt(IV), the separation parameters of Pd(II) and Pt(IV), including dibutyl sulfoxide concentration, contact time of aqueous and organic phases, organic/aqueous (O/A) phase ratio and H+ concentration of aqueous phase, were studied in detail, and the optimal separation parameters were obtained and summarized as the following: dibutyl sulfoxide concentration 0.6–1.2 mol dm-3, organic/aqueous (O/A) phase ratio 0.6–1.0, H+ concentration of aqueous phase 1.0–1.5 mol dm-3 and contact time of two phases 5 min. The as-prepared separation parameters were corroborated by the extraction and separation from a synthetic stock solution containing Pd(II), Pt(IV) as well as several common impurities like Fe(II), Cu(II) and Ni(II). The results revealed that Pd(II) could be separated efficiently from Pt(IV) with a high separation coefficient of Pd(II) an Pt(IV) (2.7 × 104) by predominantly controlling dibutyl sulfoxide and hydrochloric acid concentrations. The extraction saturation capacity of Pd(II) was determined from 1.0 mol dm-3 HCl solution with 3 mol dm-3 dibutyl sulfoxide and its experimental value exceeded 14 g dm-3 under the experimental conditions. Stripping of Pd(II) from loaded organic phase was performed using a mixed aqueous solution containing NH4Cl and ammonia solutes. Pd(II) (99.2%) was stripped using the stripping solution containing 3% (m/v) NH4Cl and 5 mol dm-3 ammonia, respectively.

**Solid-phase extraction methods**

Solid-phase extraction methods have also been incorporated into PGM refineries recently, either to compliment or replace solvent extraction methods. Solid-phase extractants have included well established commercial anion-exchange resins such as Amberlite IRA 400 (Sigma-Aldrich company), as well as proprietary media such as the Superlig series of media. The latter series makes use of cation and anion selective ligands which are covalently bonded to solid supports. Use of a series of different Superlig media has been proposed for the extraction and separation of Pd, Pt and Rh in consecutive stages (Figure 14). Mechanisms of separation for the Superlig media include ligand exchange (Pd extraction) or ion-exchange ([PtCl6]2 extraction), however in each case selectivity has been attributed to a high level of molecular recognition. Analogous to solvent extraction both scrubbing and stripping stages are required in separations involving solid phase extraction media (Bernardis et. al., 2005).
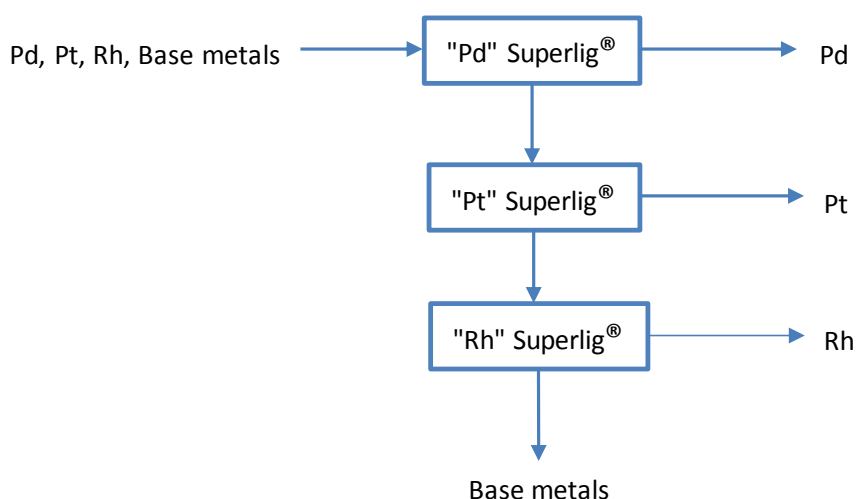


Fig.14 Separation of Pd, Pt and Rh from chloride media using Superligmedia

The investigation (O.N. Kononova et al., 2010) is devoted to sorption recovery of platinum (II, IV) from chloride solutions, freshly prepared and kept over 3 months, on commercial anion exchangers with different physical and chemical structure. The resins were chosen for their good sorption properties for other noble metal systems (gold, silver and palladium) in our previous investigations. The concentration of platinum in initial solutions was 0.25–1.0 mmol/L, whereas hydrochloric acid concentration varied from 0.01 to 4 mol/L. It was shown that anion exchangers investigated possess high sorption ability to chloride complexes of platinum (II, IV). These sorption characteristics do not deteriorate in case of noble metals recovery from kept solutions.

Batches of authentic industrial base metal refinery (BMR) and precious metal refinery (PMR) effluents containing large amounts of Ni, Cu and Fe ions and relatively small amounts of the valuable Pt, Pd and Rh metal ions have been treated with silicabased (poly)amine anion exchangers. In most cases, notably with the PMR effluents, the extraction of Pt and Pd appeared to be very effective, with recuperation of more than 95% from some of the effluents, while an increase in temperature was not necessary to obtain maximum metal ion uptake. Successive Rh extraction from the BMR effluents resulted in a maximum removal of 22% of the metal ions initially present. A higher percentage could not be reached apparently due to the presence of large amounts of competing sulphate and chloride counter ions. The removal of Rh from PMR effluents containing smaller amounts of other transition metal ions was somewhat more effective. Despite the large amounts of Ni,

Cu and Fe in many of the tested effluents, no uptake of any of these metal ions has been observed. The platinum group metal (PGM) selectivity of these ion exchangers over the other transition metals has thus proven to be very high (Jurjen Kramer et al.,2002).

**Refining trends and prospects**

Research and development in the field of PGM refining will always be fuelled by **potential economic gains**, which arise from new faster, simpler and more efficient refining methods. Of increasing importance however, is the need for processes which **reduce harm to the environment**. Large benefits have been realised in moving from classical precipitation methods to solvent and solid phase extraction methods and the design of more selective extractants will no doubt continue to be pursued with ever-increasing sophistication. Isocratic elution chromatography does potentially offer refiners greater simplicity in the form of a unit process. Much research and development in the field of polymer supports has taken place over the latter half of the century albeit mostly for the rapidly growing biological separations industry. Through use of this know-how and a knowledge of PGM chemistry, considerable potential remains for researchers to become involved in the science and technology of specific PGM separations (Bernardis et. al.,2005).

## 21.3 TECHNICAL INNOVATIONS IN PGM PRODUCTIONS FROM PRIMARY RESOURCES

### 21.3.1 MINERAL PROCESSING

The Use of Centrifugal Gravity Concentrators

Knelson and Falcon type centrifugal-type concentrators are being tested in a number of applications in a number of operations. The Noril'sk mining company reports that up to 60% of the Pt and 13% of the Pd were recovered in the gravity concentrator. The grade of the concentrate was 400 to 500 g/t PGE. The equipment was tested on the disseminated ore with a feed grade of between 4.5 to 5.9 g/t Pt and Pd (Cole and Ferron, 2002-03).

The Use of Dense Media Separation

Dense media separation is being used to upgrade UG2 ores prior to milling. This enables miners to use wide reef mining techniques, substantially reducing mining costs. The chromite reef is removed from the lower density country rock. The most recent example of this type of installation is the new Kroondal mine. The technology is being considered for the Impala Winaarshoek project, scheduled for construction in the first part of 2002 (Lawrence, 2001).

The Use of Large "Tank" Type Flotation Cells

More and more producers are using large tank type cells in new installations and plant upgrades. The motivation behind moving to the larger cells is largely driven by lower capital and operating costs associated with using large equipment, rather than many smaller units. Although subjective, it is possible that simplifying the process and reducing the number of streams that an operator will need to monitor can improve the overall metallurgical performance of a flowsheet. The rationale behind this thinking is that the operators will dedicate more time to each circuit as a whole and thus improve operational response to the ore. Examples of large tank

cell installations are the Impala Merensky plant that has 18 x 130 m$^3$ tank cells in the rougher circuit and the new Lac des Iles concentrator that has 14 x 130 m$^3$ tank cells in the scavenger circuit.

Diagnostic Metallurgy and the Role of Process Mineralogy

Detailed size-by-size analysis encompassing both metal and mineralogical balances of gangue, sulphide and platinum group minerals is helping the industry to build a detailed database of metal loss to tailings. Although these investigations are time consuming and costly, the benefits far outweigh the costs. Technology and methods to improve analysis time are actively being pursued. In South Africa, the platinum industry is known to use SEM-based imaging technology to significantly improve both final recovery and final concentrate grade in their concentrates. This technology is also used in Canada for Ni-Cu ores, for example, at Falconbridge.

Ultrafine grinding

Recent test work has focused on ultra fine grinding of the cleaner tailings followed by flotation. It has been reported that the newly liberated PGM and base metal sulphides exhibit high flotation recoveries and that the cleaner tails can often be open-circuited. A further advantage of open-circuiting is that additional residence time is gained on the rougher bank by not re-circulating the cleaner tail. One South African PGE producer has reported obtaining upgrade ratios of more than 60 when grinding cleaner tails from a P50 of 18.6 µm to a P50 of 7.1 µm. Recoveries of PGE from the tails doubled. It should be noted that energy requirements for this size reduction are very high at approximately 60 kWh/t (Goodall et al., 2001).

Circuit Simulation and Optimization

The platinum producers in South Africa have been actively involved with the Amira P9 project to gain a deeper understanding of the fundamentals that govern flotation performance. One part of the flotation research module in which the Julius Kruttschnitt Mineral Research Centre (JKMRC) and the University of Cape Town (UCT) collaborate is the Flotability Characterization Test Rig (FCTR). The FCTR is essentially a portable pilot plant with monitoring equipment that is used to evaluate circuit changes, design concepts and trial equipment. The test rig includes equipment needed to gather data required to model the system being tested. The model is validated against the "pilot plant" data obtained from the FCTR. (JC World, 2001).

Froth Imaging

A number of groups are working on froth imaging or "machine vision" systems. The objectives are to capture data such as the average grey level and froth structure and to correlate the parameters with the metallurgical performance of the flotation process. The effect of process parameters such as conditioning time, and intensity as well as reagent additions on the froth structure has been studied and correlated to the froth structure and metallurgical performance. (Moolman et al., 1996) (Aldrich et al., 1997).

## 21.3.2 METALLURGICAL EXTRACTION

New Leaching Technologies

At elevated temperatures between 120 and 180 °C, PGMs can be leached by sodium cyanide like the reaction of gold. A new technique to treat Pt–Pd sulfide flotation concentrates and spent auto-catalysts by pressure cyanidation is put forward, and the results of 5 kg-scale batch experiments in a 50 L autoclave are reported for process development. The cyanide leaching reaction mechanism is also discussed. For flotation concentrates

containing about 80 g/t Pt and Pd, after pre-treating by pressure acid leaching, followed by two steps of pressure cyanide leaching, up to 90–94% Pt and 99% Pd extraction could be achieved. Final concentrates .obtained from cyanide leaching solution using zinc cementation contained 70– 90% of precious metals. For spent auto-catalysts containing ≈1000 – 2000 g/t Pt+Pd+Rh, after a pre-treatment process to remove the wrapping of the catalyst carrier and to rid surface accumulated carbon and gasoline contaminants, followed by two steps of pressure cyanide leaching, the recoveries of Pt, Pd and Rh were 95–96%, 97–98% and 90–92%, respectively (Chen and Huang, 2006).

Direct Leaching of PGE Ores/Concentrates

The present-day technology to treat high-grade PGE concentrates (smelting to matte, Base Metals Refinery) performs well and is well established. There are a few situations, however, where it is not suitable:

The concentrate is too low grade or contains too many deleterious minerals for the smelter (i.e. Cr2O3, MgO, As, etc); The mine is remote and transportation costs to a centralised smelter would be prohibitive; Smelter contracts are not favourable to small operators.

Because of these potential issues, much effort has been devoted to develop alternative process routes (Table 4).

Table 4 Alternative process routes

| Technology | | |
|---|---|---|
| BHP TML Process | To recover PGE from the oxidised portion of the Hartley deposit in Zimbabwe: Roasting: 300-700ºC with air, H2SO4 Leaching (70ºC), 10 g/L NaBr as oxidant. Recoveries were 90% Au, 85% Pt and 70% Rh | Duyvesteyn et al., 1994 |
| North American Palladium Process | For the treatment of the Lac des Isles PGE concentrate (4-6 g/t Au, 4-6 g/t Pt, 50-80 g/t Pd, 2.5-3.0% Cu, 1.8 - 2.5% Ni, 12-12.5% Fe and 6-8% S): Partial oxidizing roast, pressure leaching (HCl/HNO3). Recoveries 95-98% Au, 94-95% Pt, 87-91% Pd, 78-96% Cu, 82-92% Ni. | McDoulett, Reschke, 1994 |
| High Temperature Cyanidation Process | The Coronation Hill (Australia) ore could not be upgraded by flotation or gravity, a cyanidation process developed by CSIRO: Grinding – amalgamation, high temperature (100-125ºC) cyanidation, followed by (Au + Pt) CIP. Extractions >95% Au, 90% Pd and 80% Pt. | Bruckard et al., 1992 |
| PLATSOL™ Process | To treat PolyMet NorthMet (formerly Dunka Road) deposit | Fleming et al., 2000; Ferron et al., 2000; Ferron et al., 2001; |

| | within the Duluth Gabbro in Minnesota, USA.<br>High temperature (>200ºC) pressure oxidation with small additions of NaCl (5-20 g/L NaCl). The base metals (Cu, Ni, Co) and the precious metals (Au, Pt, Pd) are dissolved in one single step. The PGE's are then recovered from solution using NaSH. | |
|---|---|---|
| Alternative reagents for the selective extraction of the PGE | Solvent extraction of rhodium from chloride solutions is greatly improved with the addition of $SnCl_2$ | Mhaske et al., 2001; Shafiqul et al., 1997 |
| Ion Exchange Resins | 1）Polyisothiourea (PITU)，chelating resins are not selective; The elutant is thiourea, and the PGE can then be separated by precipitation or solvent extraction.<br>2）Amborane Resins, mildly reducing agents (amine-boranes), reacting with the precious metals to produce boric acid and metallic precious metal covering the polymer bead.<br>3) SuperLig, molecular recognition ligands (MRT)<br>Tanaka Kikinzoku Kogyo (TKK) precious metal refinery recovers rhodium from the refinery feedstream containing PGE and base metals, using five columns in series of SuperLig 96. In 1997, Impala installed a MRT system for the separation and purification of Pd in their primary PGE refinery<br>4) Resin TP-207, a selective resin, normally sold as a sodium salt of the iminodiacetic acid functional group. has been piloted by Noranda to recover Pd from Moebius cell electrolyte. During silver electrorefining, Pd and Cu dissolve and accumulate in the nitrate electrolyte, and a bleed is | Warshawsky, 1983; Demopoulos, 1989; Ruckman, 1989; Robinson, 1995; Van Tonder et al., 2001; Rosato, Shink, 1989 |

| | | |
|---|---|---|
| | required to control the build-up of these elements and maintain silver purity. | |

Recovery of platinum (Pt) and palladium (Pd) through biosorption

Biosorption represents a biotechnological innovation as well as a cost effective excellent tool for recovery of precious metals including platinum and palladium from aqueous solutions. Nilanjana Das (2010) reviewed the investigations in recent years on recovery of platinum (Pt) and palladium (Pd) through biosorption. Guibal et al. (1999b) studied the recovery of platinum ions from dilute solutions by chitosan cross linked with glutaraldehyde. Godlewska -Zylkiewicz and Kozlowska (2005) reported the binding of Pt and Pd by Saccharomyces cerevisiae. Immobilised Chlorella vulgaris has also been studied as a Pt and Pd biosorbent (Dziwulska et al., 2004). The adsorption of Pt (IV) and Pd (II) on bayberry tannin immobilized collagen fiber (BTICF) membrane was investigated by Ma et al. (2006).

The adsorption capacities of Pt (IV) and Pd (II) on 0.100 g BTICF membrane were 41.7 and 27.5 mg/g at 313 K. Crosslinked chitosan resin chemically modified with l-lysine has been used to investigate the adsorption of Pt (IV) and Pd (II) from aqueous solutions (Fujiwara et al., 2007). The maximum adsorption capacity was found to be 129.26 mg/g for Pt (IV) and 109.47 mg/g for Pd (II).

Recovery of platinum by a high performance biosorbent, polyethylenimine (PEI)-modified biomass, prepared by attaching PEI onto the surface of inactive Escherichia coli biomass was reported by Won et al. (2010). Wastewater collected from an industrial laboratory for inductively coupled plasma (ICP) using PEI modified biomass was studied. The maximum platinum uptake of PEI-modified biomass was enhanced up to 108.8 mg/g compared to 21.4 mg/g of the raw biomass.

Recently, the biosorption potential of Racomitrium lanuginosum as aquatic moss biosorbent for the removal of Pd (II) from aqueous solution has been reported (Sari et al., 2009). The adsorption capacity of barley straw carbon for Pt (IV) and Pd (II) has been found to be 0.39 and 0.64 mmol /kg (Chand et al., 2009).

The important factors influencing batch biosorption of precious metals including solution pH, temperature, biomass dosage, ionic strength, initial solute concentration and agitation rate. The different types of adsorbents used for platinum and palladium biosorption are summarized in Tables 5 and 6 (Nilanjana Das, 2010).

Table 5 Biosorption of platinum ($Pt^{4+}$) using different adsorbents.

| Adsorbents | pH | $Q_{max}$ (mmol/g) |
|---|---|---|
| Bacteria | | |
| Desulfovibrio desulfuricans | 2.0 | 0.32 |
| Desulfovibrio fructosivorans | 2.0 | 0.17 |
| Desulfovibrio vulgaris | 2.0 | 0.17 |
| | | |
| Others | | |
| Bayberry tannin immobilized | 3.0 | 0.23 |
| Collagen fiber (BTICF) membrane | | |
| Thiourea derivative of chitosan | 2.0 | 2.0 |
| Glutaraldehyde crosslinked chitosan | | |

| Chitosan derivatives | | |

Table 6 Biosorption of palladium (Pd2+) using different adsorbents.

| Adsorbents | pH | $Q_{max}$ (mmol/g) |
|---|---|---|
| Bacteria | | |
| Desulfovibrio desulfuricans | 2.0 | 1.2 |
| Desulfovibrio fructosivorans | 2.0 | 1.0 |
| Others | | |
| Aquatic moss (Racomitrium lanuginosum) | 5.0 | 37.2 mg/g |
| Bayberry tannin immobilized Collagen fiber (BTICF) membrane | 4.0 | 0.32 |
| Chitosan derivatives | 2.0 | 3.5 |
| Rubeanic acid derivative of chitosan | 2.0 | 3.24 |
| Thiourea derivative of chitosan | 2.0 | 2.54 |
| Glutaraldehyde crosslinked chitosan | 2.0 | 2.44 |

Compared with the conventional methods, a biosorption-based process offers a number of advantages including low operating costs, minimization of the volume of chemical and/or biological sludge to be handled and high efficiency in detoxifying effluents, and it would guarantee a strong penetration of large market for precious metal recovery in future (Nilanjana Das, 2010).

## 21.4 CHARACTERIZATION OF MINING TAILINGS AND PROCESSING RESIDUES AND POTENTIAL UTILIZATIONS

### 21.4.1 PGMS CONTAINING TAILINGS FROM CHROMIUM MINES IN SOUTH AFRICA

Flotation tailings from the Northam Platinum Limited plant operations

There are over 450 million tonnes of flotation tailings and smelter slags containing appreciable amounts of PGMs in South Africa (J. Siame, and H. Kasaini, 2013). The average grade of total PGMs in tailings vary from one mining firm to another. The average PGM recoveries on concentrator feed solids vary between 80 and 88% across the industry and depending on the feed grade (4–8 g/t); the final flotation tailings may contain significant amounts of PGMs (0.7–1.6 g/t). Beneficiation of PGM tailings by further flotation has limited benefits since only about 30% of PGMs are associated with base-metal sulphides and the rest are either inclusions or attached to clay minerals, with a small fraction being free or native minerals of PGMs. Fine grinding is required to liberate the PGMs which are locked in either chromite matrix or silicates (C. J. Penbertny et al., 2000). Owing to the mineral hardness of silicates and chromite (5–6 Mohs scale) energy consumption in the milling process is expected to be high.

The economic mineral reserves for PGMs are found in the Busheveld Complex geological formation of South Africa particularly in the narrow strata of Merensky Reef, (Platreef) and the UG2 chromitite layer. The major minerals in UG2 flotation tailings are chromite {$FeCr_2O_4$, S.G = 4.5 – 4.8}, orthopyroxene {$(Mg, Fe)_2Si_2O_6$, S.G = 3.2 – 3.9} and plagioclase {$Na_{0.5}Ca_{0.5}Si_3AlO_8$, S.G = 2.6 – 2.8} with small amounts of talc {$Mg_3Si_4O_{10}(OH)_2$, S.G = 2.7 – 2.8} and clay minerals (chlorites/phlogopite, S.G = 2.2 – 2.75). PGMs in flotation tailings are either

associated with silicates (60%) or are free PGMs particles (10%) while 30% of them are associated with sulphide minerals (pentlandite, chalcopyrite, pyrrhotite pyrite and millerite). On the basis of mineralogical data, about 70% of total PGMs associated with silicates and native alloys can be separated from oxide and sulphide minerals using gravity separators (J. Siame, and H. Kasaini, 2013).

Mineralogical data on UG2 samples was generated by means of MLA technique. The UG2 samples are flotation tailings from the Northam Platinum Limited plant operations in South Africa. Table 7 illustrates the mineralogical profile of UG2 flotation tailings which contain about 0.7 g/t, total PGMs (Northam Platinum Ltd.). The most floated PGMs are associated with metal oxides and sulphides while PGMs enclosed or attached to silicates are lost to the tailings together with significant amount of free PGM particles. The particle size and PGMs distributions of the tailings are shown in Table 8. The 43% of PGMs are distributed in the fine (-45μm) fraction.

Table 7 Mineralogical data on UG2 tailings

| Minerals | PGM Distribution | |
|---|---|---|
| Oxides | Enclosed | 2% |
| Silicates | Association | 25% |
| | Attached | 21% |
| | Enclosed | 11% |
| Sulphides | Association | 26% |
| | Attached | 2% |
| | Enclosed | 2% |
| Free or Native Minerals | Free | 13% |

Table 8 PSD of tailings and PGMs distribution

| Size fraction (μm) | Wt. %, solids | PGMs Distribution (%) |
|---|---|---|
| +106 | 33 | 30 |
| -106 +75 | 15 | 14 |
| -75 +45 | 17 | 13 |
| -45* | 35 | 43 |

Tailings dumps of the chromium mines in the Bushveld Complex

Although the concentration of platinum-group elements in the LG-6 Chromitite Layer is very low (about 0,5 g/t) the minerals that contain these elements occur largely between the chromite grains. Because of their small grain size, these minerals, during the washing of the ore, become concentrated together with the silicate impurities in the tailings. The platinum-group elements in the tailings are such that their extraction appears to be a highly profitable exercise. It is estimated that the tailings dumps of the chromium mines in the Bushveld Complex contain close to 400,000 oz of PGMs, to which about 38,000 oz are added annually (Gruenewaldt and Hatton, 1987).

Table 9 Analyses of samples from the tailings dumps of chromium mines on the Bushveld Complex

| Sample | Pt | Pd | Rh | Ru | Total PGE | Cu | Ni |
|---|---|---|---|---|---|---|---|
| 1 | 3.2 | 2.03 | 0.35 | 3.4 | 8.98 | 130 | 195 |
| 2 | 4.52 | 2.8 | 0.45 | 2.63 | 10.4 | 95 | 264 |
| 3 | 3.06 | 1.4 | 0.16 | 1.43 | 6.05 | 69 | 119 |
| 4 | 3.17 | 0.93 | 0.18 | 2.14 | 6.42 | 50 | 439 |
| 5 | 0.25 | 0.11 | 0.06 | 0.6 | 1.02 | 17 | 78 |

| 6 | 0.99 | 0.45 | | | >1.44 | 40 | 282 |
|---|------|------|------|------|-------|----|-----|
| 7 | 0.42 | 0.27 | 0.03 | 0.73 | 1.45 | 20 | 86 |
| 8 | 0.57 | 0.4 | 0.07 | 1.11 | 2.15 | 35 | 126 |
| 9 | 1.13 | 0.36 | 0.07 | 0.61 | 2.17 | 29 | 95 |

The analyses of samples from the tailings dumps of chromium mines on the Bushveld Complex are shown in Table 9. The high grade of the tailings produced by thorough washing of the chromitite from the LG-6 Layer is such that the recovery of the PGE appears to be a profitable exercise that could be accomplished with a relatively small capital outlay. However, the scattered nature of the deposits and the low tonnage at each mine would require several small-scale operations to produce flotation concentrates for further processing of the PGE. For the poorly separated LG-6 tailings, a combined programme of PGE and chromite extraction could, in sum, also be a profitable venture. However, it must be emphasized that the figures mentioned in this report are based on limited observations, and that considerably more data would be required for a proper evaluation. Research required to ensure the optimal recovery of the PGM from the tailings should include, inter alia, studies of the type, grain size, and mode of occurrence of the PGM in the tailings, which would indicate whether additional milling is required to liberate the PGM from the silicates, and which flotation reagents are required to ensure maximum recovery. A study of the vertical distribution of the PGE in the LG-6 and MG-l Chromitite Layers would show whether or not these elements have a distribution analogous to those in the UG-2 Chromitite Layer, where distinct peaks of mineralization occur at specific levels within the layer. Such knowledge could be of use in selective mining and beneficiation of the ore (Gruenewaldt and Hatton, 1987).

<u>The tailings from Anglo Platinum's Waterval concentrator operations</u>

Platinum Mile operates a flotation plant treating the tailings from Anglo Platinum's Waterval concentrator operations. The contained PGMs and base metals are recovered as a low grade flotation concentrate and are further treated for the recovery of saleable metals at Anglo Platinum's integrated downstream smelting and refining operations in Rustenburg. To improve the financial returns of the Pt Mile operation and to gain operating data and experience; Pt Mile and Anglo Platinum agreed to a collaborative investigation of concentrate ultra fine grinding (UFG) at the Pt Mile plant (Rule et al.,2008).

Anglo Platinum loaned a 355 kW Metso SMDTM unit and proposed a joint investigation programme at the Pt Mile plant, after consideration and discussion of initial promising laboratory - scale work conducted by Pt Mile at Mintek.

The plant treats two streams separately, a UG2 stream and a mixed UG2 and Merensky stream. These are respectively, the final tails from the Waterval UG2 Concentrator, with a capacity of 485 000 tpm, and the final tails stream from the Waterval Merensky Concentrator, with a capacity of 460 000 tpm. (Subsequently this plant became the Waterval Retrofit Concentrator in third quarter 2007, with a maximum capacity of 620 000 tpm.) The tailings from the Waterval Smelter slag treatment plant is co-processed with arisings from the retrofit plant.
The feed to the plant is low grade, generally less than 0.8 ppm 4T PGM (4T refers to platinum, palladium, rhodium and gold content) and consists, in the majority, of slow floating value mineral species. Table I is a typical composite sample for plant feed to the Merensky stream at Platinum Mile's plant; the majority of recovered PGMs is from this stream.
The plant is sited adjacent to the Paardekraal booster pump station, on the corner of the Paardekraal tailings dam complex. Feed and tails to and from the plant are delivered from and returned to the booster station for onward deposition.

The plant is sited adjacent to the Paardekraal booster pump station, on the corner of the Paardekraal tailings dam complex. Feed and tails to and from the plant are delivered from and returned to the booster station for onward deposition.

The mineralogical data shows the very fine grain size of PGMs in Platinum Mile feed and the marked distribution of middlings and locked PGMs in the +10 and +25 micron fractions. Clearly, fine grained PGMs are recoverable even when they are not fully liberated. Hence the potential for improving concentrate grade is evident; by the application of fine grinding to liberate locked and middling PGMs in composite silicate gangue particles.

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## 22 RARE EARTH ELEMENTS (REE)

### 22.1 PRODUCTION LINES OF IDENTIFICATION FROM PRIMARY RESOURCES

#### 22.1.1 REE, PRODUCTION AND APPLICATIONS

The rare earth elements (REE), also called the rare earth metals (REM), normally refer to the fifteen metallic elements of the lanthanide series, coupled with the chemically similar ytrrium and/or scandium (Gupta and Krishnamurthy, 2005; Jordens et al., 2013; Zepf, 2016). REE are typically split into two sub-groups, the light rare earth elements (LREE), also known as the cerium group, which includes Sc, La, Ce, Pr, Nd, Pm, Sm and Eu, and the heavy rare earth elements (HREE), also known as the yttrium group, which includes Y, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu (Jordens et al., 2013).

In the 1950s the global production of rare-earth oxides (REO) reached about 1000 t and doubled in 1960. In 1970 the production grew to 16,000 t; in 1980 to 27,000 t; in 1990 to 53,000 t; and in 2000 to 90,000 t, reaching two peaks in 2006 and 2009 at 137,000 and 135,000 t, respectively (Zepf, 2016). Since 2009, the global production declined (Zepf, 2016). In 2013 it was 110,000 t. Since 2014 the production had kept stable, 123,000 t in 2014 (USGS, 2016), 130,000 t in 2015 and 126,000 t in 2016 (USGS, 2017). In addition to these numbers, considerable illegal mining is present.  Annual illegal production was estimated to be 40,000 t (Zepf, 2016).

REE have various of industrial applications. REO used in mature markets such as catalysts, glassmaking and metallurgy account for 59% of the total worldwide consumption, and in newer, high-growth markets such as battery alloys, ceramics, and permanent magnets account for 41% of the total worldwide consumption. The main industrial applications of REE are briefly listed in Table 1 (Charalampides et al., 2015). And the share of REE in various application areas is shown in Table 2 (Zepf, 2016).

Table 1. Main industrial applications of REE

| REE | Application |
|---|---|
| Scandium (Sc) | High-strength Al-Sc alloys, electron beam tubes |
| Yttrium (Y) | Capacitors, phosphors, microwave filters, glasses, oxygen sensors, radars, lasers, superconductors |
| Lanthanum (La) | Glasses, ceramics, car catalysts, phosphors, pigments, accumulators |
| Cerium (Ce) | Polishing powders, ceramics, phosphors, glasses, catalysts, pigments, misch metal, UV filters |
| Praseodymium (Pr) | Ceramics, glasses, pigments |
| Neodymium (Nd) | Permanent magnets, catalysts, IR filters, pigments for glass, lasers |
| Promethium (Pm) | Sources for measuring devices, miniature nuclear batteries, phosphors |
| Samarium (Sm) | Permanent magnets, microwave filters, nuclear industry |
| Europium (Eu) | Phosphors |
| Terbium (Tb) | Phosphors |

| | | |
|---|---|---|
| Dysprosium (Dy) | Phosphors, ceramics, nuclear industry | |
| Holmium (Ho) | Ceramics, lasers, nuclear industry | |
| Erbium (Er) | Ceramics, dyes for glass, optical fibers, lasers, nuclear industry | |
| Ytterbium (Yb) | Metallurgy, chemical industry | |
| Lutecium (Lu) | Single crystal scintillators | |
| Thulium (Tm) | Electron bean tubes, visualization of images in medicine | |
| Gadolinium (Gd) | Visualization of images in medicine, optical and magnetic detection, ceramics, glasses, crystal scintillators | |

Table 2. Share of REE in various application areas is shown in Table 2 (Zepf, 2016).

| | La (%) | Ce (%) | Pr (%) | Nd (%) | Sm (%) | Eu (%) | Gd (%) | Tb (%) | Dy (%) | Y (%) | Check Sum | Demand Estimate (2010) (%) | Production Estimate: 134,000 t REO (2010) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Permanent magnets | | | 23 | 69 | | | 2 | 1 | 5 | | 100 | 24 | 32,160 |
| Phosphors | 9 | 10 | | | | 5 | 2 | 5 | | 69 | 100 | 6 | 8040 |
| Battery alloy | 50 | 34 | 3 | 10 | 3 | | | | | | 100 | 12 | 16,080 |
| Fluid catalytic cracking | 90 | 10 | | | | | | | | | 100 | 16 | 21,440 |
| Ceramics | 17 | 12 | 6 | 12 | | | | | | 53 | 100 | 1 | 1340 |
| Glass additives | 24 | 66 | 1 | 3 | | | | | | 2 | 96 | 8 | 10,720 |
| Polishing powders | 31 | 65 | 4 | | | | | | | | 100 | 15 | 20,100 |
| Auto catalysts | 5 | 90 | 2 | 3 | | | | | | | 100 | 7 | 9380 |
| Metallurgy | 26 | 52 | 5 | 17 | | | | | | | 100 | 9 | 12,060 |

## 22.1.2 PRIMARY RESOURCES FOR REE PRODUCTION

The abundances of some of the REE in the earth's continental crust are very low but not as low as the rarest elements such as goled, mercury and indium. Seven of the REE have abundances comparable with those of other imporatnat economic elements (1-10 µg/g) which are not considered to be particularly rare, such as tungsten, tin, arsenic and bromine. Four of the REE have abundances between 15 and 100 µg/g along with the elements copper, cobalt, rubidium and zinc. Ce at an estimated concentration of about 30 µg/g is the most abundant REE in the crust (Henderson, 1996).

Rare-earth bearing minerals can be classified into the following six types based on the types of anionic groups in their crystal structures (Miyawaki and Nakai, 1996).

1. minerals with crystal structures containing isolated triangular anionic groups – carbonates: e.g. lanthanite [$La_2(CO_3)_3 \cdot 8H_2O$] and bastnäsite-(Ce) [$Ce(CO_3)F$];
2. minerals with crystal structures containing only isolated tetrahedral anionic groups – phosphates: e.g. xenotime-(Y) [$YPO4$] and monazite-(Ce) [$CePO4$];
3. minerals with crystal structures containing anionic groups of tetrahedral ions – silicates: e.g. thalenite-(Y) [$Y_3Si_3O_{10}(OH)$] and cerite-(Ce) [$Ce_9(, Ca)(Fe, Mg)(SiO_4)_6(SiO_3OH)(OH)_3$];
4. minerals with crystal structures containing anionic groups of tetrahedral and octahedral ions – aluminosilicates and titanosilicates: e.g. allanite-(Ce) [$Ca(Ce,Ca)Al(Al,Fe)(Fe,Al)(Si_2O_7)(SiO_4)O(OH)$] and mosandrite [$Na(Na,Ca)_2(Ca,Ce)_4(Ti,Nb,Zr)(Si_2O_7)_2(O,F)_2F_2$];
5. minerals with crystal structures containing anionic groups of octahedral ions – titanates and niobates: e.g. aeschynite-(Ce) [$(Ce,Ca,Fe,Th)-(Ti,Nb)_2(O,OH)_6$] and fergusonite-(Y) [$YNbO4$];
6. minerals with crystal structures without anionic groups – fluorides and simple oxides: e.g. fluocerite-(Ce) [$CeF_3$] and cerianite-(Ce) [$(Ce,Th)O_2$].

Nearly 200 minerals have been found to contain >0.01% REE. Most of them are rare and commercially economical REE minerals may be only about 10 to 20 including bastnäsite, monazite, xenotime, steenstrupine, parisite, apatite, eudialyte, allanite, pyrochlore and zircon etc. RE minerals are found in hard rock (primary origin) and placer deposits (secondary origin) throughout the world.

Well-known minerals containing cerium and the light lanthanides include bastnäsite, monazite, allanite, loparite, ancylite, parisite, lanthanite, chevkinite, cerite, stillwellite, britholite, fluocerite, and cerianite.

Bastnäsite and monazite are the most important RE minerals In the 103 REE deposits in the world 78 are the deposits of monazite (57 placer and 21 hard rock) and 11 are the deposits of bastnäsite. The 77% of total REO occurs in bastnäsite, 19% in monazite and only 3% in other minerals (Jakson and Christiansen, 1993). Bastnäsite (rocks from several locaties in China such as Bayan Obo and Mountain Pass, California), monazite (marine sands from Brazil, India, and Australia; rocks from Bayan Obo, China, and South Africa), and loparite (rock from Kola Peninsula, Russia) have been the principal sources of cerium and the light lanthanides. It was estimated the world RE production in 1989 at 50,000 t of REO with 50% composed by bastnäsite, 40% by monazite, and the balance mainly from the ion adsorption ores in China. By 2002 over 80% of all REO produced is from bastnäsite, about 10% from ion adsorption ores, 5% from monazite and the remaining from other sources such as xenotime, loparite, and brannerite (Gupta and Krishnamurth, 2005; Papangelakis and Moldoveanu, 2014).

Thus, among the anhydrous rare earth phosphates, it is the tetragonal mineral xenotime that incorporates yttrium and the yttrium earths, whereas the monoclinic monazite phase incorporates cerium and the cerium earths preferentially. The smaller size of the yttrium group allows it a greater solid solubility in the rock-forming minerals that comprise Earth's mantle, and thus yttrium and the yttrium earths show less enrichment in Earth's crust relative to chondritic abundance, than does cerium and the cerium earths. This has economic consequences: large ore bodies of the cerium earths are known around the world, and are being exploited. Corresponding orebodies for yttrium tend to be rarer, smaller, and less concentrated.

Most of the current supply of yttrium originates in the "ion absorption clay" ores from Southern China. Some versions provide concentrates containing about 65% yttrium oxide, with the heavy lanthanides being present in ratios reflecting the Oddo-Harkins rule: even-numbered heavy lanthanides at abundances of about 5% each, and odd-numbered lanthanides at abundances of about 1% each. Similar compositions are found in xenotime or gadolinite.

It is reported (Powell, 2011) in Nature Geoscience that rare earth resources undersea are much more promising than on-land resources, concentrations of rare earths were comparable to those found in clays mined in China. Some deposits contained twice as much heavy rare earths such as dysprosium.

Mine tailings and processing residues are potential sources for REE production. Significant quantities of rare earth oxides are found in tailings accumulated from 50 years of uranium ore, shale and loparite mining at Sillamäe, Estonia (Rofer and Kaasik, 2000). The country currently exports around 3,000 tonnes per year, representing around 2% of world production (Reigas, 2010). Similar resources are suspected in the western United States, where gold rush-era mines are believed to have discarded large amounts of rare earths, because they had no value at the time (Cone, 2013). Phosphogypsum (PG) is an acidic by-product from the phosphate fertilizer industry. PG is considered a potentially valuable source of the rare earth metals. It was estimated that 170 or even 280 million tonnes of PG were produced annually. If assume the average content of REE in the PG being 500 pm (this is reasonable) the potential source of REE from the PG would be annually 85,000 - 140, 000 t. It was estimated that in Florida alone, approximately 30,000 t of rare earth elements are discarded with various phosphate mining waste by-products annually (Zhang 2014).

Nuclear reprocessing is another potential source of rare earth or any other elements. Nuclear fission of uranium or plutonium produces a full range of elements, including all their isotopes. However, due to the radioactivity of many of these isotopes, it is unlikely that extracting them from the mixture can be done safely and economically.

In January 2013 a Japanese deep-sea research vessel obtained seven deep-sea mud core samples from the Pacific Ocean seafloor at 5,600 to 5,800 meters depth, approximately 250 kilometres (160 mi) south of the island of Minami-Tori-Shima (Nikkei Inc., 2014). The research team found a mud layer 2 to 4 meters beneath the seabed with concentrations of up to 0.66% rare earth oxides. A potential deposit might compare in grade with the ion-absorption-type deposits in southern China that provide the bulk of Chinese REO mine production, which grade in the range of 0.05% to 0.5% REO (University of Tokyo, 2013; Li and Yang, 2014).

Another recently developed source of rare earths is electronic waste and other wastes that have significant rare earth components. New advances in recycling technology have made extraction of rare earths from these materials more feasible (International, 2017) and recycling plants are currently operating in Japan, where there is an estimated 300,000 tons of rare earths stored in unused electronics (Tabuchi, 2010). In France, the Rhodia group is setting up two factories, in La Rochelle and Saint-Fons, that will produce 200 tons of rare earths a year from used fluorescent lamps, magnets and batteries (Rhodia.com., 2011; International, 2017).

China's Rare Earth Resources and Production

China has the largest resource of rare earth elements (REE) in the world. According to USGS Mineral Commodity Summaries in 2014 and 2015 the rare earth reserves in the world are around 130 to 140 million tons (Mt) (REO) and the reserves in Chin are 55 Mt (REO) which consists of 39 to 42% the world rare earth reserves (USGS 2014,2015).

Chinese rare earth resources are mainly divided into four types of deposits which consist of 95% total rare earth resources of China. They are the Bayan Obo REE–Fe–Nb ore deposit in Inner Mongolia, the Mianning rare earth ore deposit in Sichuan Province, the Weishan rare earth ore deposit in Shandong Province and the weathered crust Elution–deposited rare earth ore (called the ion adsorption type rare ore) mainly found in Jiangxi Province, but also distributed in Guandong, Fujian and Guanxi Provinces. Additionally, Southeast China beach placer deposits contain monazite and xenotime occur along the coastal area of west Guangdong and

Hainan. The average grade of placer deposits in China is 0.5 to 1.0 wt% REO. Currently, the rare earth supply in China mainly comes from above deposits.

China's rare earth presents a "light north, heavy south" pattern (Information Office of the State Council The People's Republic of China 2012). The distributions of rare earths in the China's rare earth ore deposits are presented in Table 3. It is observed that high percentages of three main light rare earths La, Ce and Nd are found in the Bayan Obo REE−Fe−Nb ore deposit, the Sichuan Mianning rare earth ore deposit and the Shandong Weishan rare earth ore deposit. However, in the ion adsorption type rare earth ores (especially type B) high contents of Y and other heavy rare earths are contained. The Bayan Obo, the Mianning and the Weishan mines are essentially producers of light rare earths and the ion adsorption rare earth deposits are basically producers of both light and heavy rare earths.

Table 3. The distributions of REO in the China's RE ore deposits

| Content of REO | Bayan Obo REE−Fe−Nb Ore (wt%) | Sichuan Mianning RE Ore (wt%) | Shandong Weishan RE Ore (wt%) | Ion Adsorption Type RE Ore | |
|---|---|---|---|---|---|
| | | | | Type A (wt%) | Type B (wt%) |
| $La_2O_3$ | $24 − 26$ | $28 − 30$ | 32 | $31 − 40$ | $2 − 5$ |
| $CeO_2$ | 50 | $45 − 50$ | $48 − 50$ | $3 − 7$ | $1 − 2$ |
| $Pr_6O_{11}$ | $3 − 5$ | 5 | 4 | $7 − 11$ | $1 − 2$ |
| $Nd_2O_3$ | $16 − 18$ | $12 − 14$ | $11 − 12$ | $26 − 35$ | $3 − 5$ |
| $Sm_2O_3$ | 1.5 | $1.5 − 2$ | $1.0 − 1.8$ | $4 − 6$ | $2 − 4$ |
| $Eu_2O_3$ | 0.2 | 0.4 | $0.1 − 0.2$ | 0.5 | 0.12 |
| $Gd_2O_3$ | 0.4 | $0.8 − 1.0$ | $0.3 − 0.5$ | 4 | 6 |
| $(Tb − Lu)_2O_3$ | $0.2 − 0.3$ | 1 | $0.4 − 0.6$ | $4 − 5$ | $15 − 20$ |
| $Y_2O_3$ | 0.3 | 0.76 | $0.1 − 0.3$ | $9 − 11$ | $>60$ |

China's rare earth production mainly takes place in Inner Mongolia, Sichuan, Guangdong, Jiangxi and Fujian. Inner Mongolia accounted for between 50 and 60 % of China's total rare earth concentrate output during the past decade. Sichuan Province was the second leading rare earth concentrate producer, accounting for between 24 and 30 % of production. The remaining output was from the provinces of Fujian, Guangdong, and Jiangxi, which are important for their production of heavy rare earths (Tse, P. 2011).

Rare earth production in China remained relatively low during 1990-1992 but started increasing from 1994. In 1995 as the leading producer, China produced 48,000 t REO (Gupta and Krishnamurth 2005). China's rare earth output as a percentage of total world output increased to more than 90 % in 2008 from 27 % in 1990. During the past 15 years, China has supplied more than 80 % of the world's rare earth as concentrates, intermediate products, and chemicals (Tse, P. 2011). China's rare earth productions (REO) from 2000 to 2014 are presented in Table 2 (USGS 2014, 2015). During years of 2000 to 2006 the rare earth production rapidly increased from 73,000 t to 133,000 t, and from 2005 to 2010 remained high at around 120,000 t. But in recent years from 2011 China's rare earth production decreased to below 100,000 t because the Chinese government has stepped up enforcement of its policies and regulations to control the rare earth production (Tse, P. 2011).

China has a complete industrial system covering mining, ore dressing, smelting and separating, as well as equipment manufacturing, material processing and end-product utilization, and China can produce over 400 varieties of rare earth products in more than 1,000 specifications. The exported rare earth products from China include rare earth oxides, rare earth salts, rare earth metals and alloys, and other (Tse, P. 2011, Information Office of the State Council The People's Republic of China 2012).

Non-Chinese capacity

A rapid expansion of non-Chinese capacity is currently proceeding. Some of the major deposits scheduled to commence production such as the Nechalacho deposit in the Northwest Territories (Canada) and Kvanefjeld (Greenland) (Adam Jordens et al., 2013). Current and potential non-Chinese REE producers are shown in Table 4 (Adam Jordens et al., 2013).

Table 4. Current and potential non-Chinese REE producers

| Company | Deposit location | Countries involved | Capacities (tpy REO) | | |
|---|---|---|---|---|---|
| | | | 2010 | 2011–2013 | Target post-2015 |
| Molycorp Minerals | Mountain Pass, CA | USA | 3000 | 40,000 | |
| Lovozersky Mining Company | Kamasurt Mine, Kola Peninsula | Russia | 3000–4400 | 15,000 | |
| Solikamsk Magnesium works | Solikamsk Processing Plant, Urals | Russia | | | |
| Indian rare earths | Orissa, Tamil Nadu and Kerala | India | 100 | 10,000 | |
| Toyota/Sojitz/Government of Vietnam | | Vietnam | 1800–2000 | >2000 | |
| Neo | | Thailand | | | |
| Lynas/Malaysia | Gebeng, Malaysia | Malaysia | | | |
| Industrias Nucleares do Brasil S/A (INB) | Buena Norte | Brazil | 1500 >1500 | | |
| Lynas Corp. | Mount Weld, Western Australia-processing plant in Gebeng, Malaysia | Australia | 10,500 | 21,000 | |
| Rareco/Great Western Minerals Group | Steenkramskaal, South Africa | South Africa/Canada | 3000 | 5000 | |
| Sumitomo/Kazatomprom/SARECO JV | Kazakhstan | Kazakhstan/Japan | 3000 | 15,000 | |

| | | | | | |
|---|---|---|---|---|---|
| Toyota/Sojitz/Government of Vietnam | Dong Pao, Vietnam | Vietnam/Japan | 300 | 5000 | |
| Toyota/Indian Rare Earths JV | Orissa, India | India/Japan | 5000 | 10,000 | |
| Mitsubishi/Neo Material Technologies | Pitinga, Brazil | Japan/USA/Canada/Brazil | 500 | 1000 | |
| Alkane Resources | Dubbo, NSW, Australia | Australia | 2600 | 6000 | |
| Avalon Rare Metals Inc. | Nechalacho deposit rich in HREEs in NWT, Canada | Canada | 0 | 5000 | |
| Quest Rare Metals | Strange Lake and others in Quebec & Labrador, Canada | Canada | 0 | 0 | |
| Ucore | Bokan–Dotson Ridge project, Alaska | USA | 0 | 0 | |
| Matamec | Kipawa deposit in Quebec, Canada | Canada | 0 | 0 | |
| Arafura | Nolan's project, Australia | Australia | 10,000 | 20,000 | |
| Great Western Minerals Group | Hoidas Lake, Canada | Canada | 3000 | 5000 | |
| Rare Element Resources | Bear Lodge, Wyoming, USA | USA | 0 | 0 | |
| Stans Energy Corp. | Kiutessay II Mine, Orlovka, Kyrgyz Republic | Kyrgyz Republic | 0 | 0 | |
| Greenland Minerals and Energy | Kvanefjeld, Greenland | Greenland | 0 | 10,000 | |
| Pele Mountain Resources | Elliott Lake, Canada | Canada | 0 | 0 | |

| Colorado Rare Earths Inc. (was US Rare Earths) | Wet Mountain/Iron Hill, USA | USA | 0 | 0 | |
|---|---|---|---|---|---|
| Namibia Rare Earths Inc. (was Etruscan Resources) | Lofdal Rare Earths Project, Namibia | Namibia, Canada | 0 | 0 | |
| Montero Mining Wigu | Hill, Tanzania | Tanzania, Canada | 0 | 0 | |
| Tasman Metals | Norra Karr, Sweden | Sweden | 0 | 0 | |
| IAMGOLD | Niobec Mine, Canada | Canada | 0 | 0 | |
| Japan–Mongolia JV | Mongolia | Mongolia | 0 | 0 | |
| Totals | | | 9500–11,000 | 37,900 | >171,500 |
| Total Projected 2015 Production from Non-Chinese Producers | | | | | 168,000 |
| Projected Demand for REEs (excluding China) | | | | | 80,000 |

*Note that projects lacking established production timelines were estimated to not be producing any REO in 2015.*

## 22.2 PROCESSING TECHNIQUES RECOGNITION AND ANALYSIS

### 22.2.1 MINERAL PROCESSING

The major REE bearing minerals that are currently exploited commercially include bastnäsite, monazite, xenotime and ion-adsorbed clays. By 2002 over 80% of all REO produced is from bastnäsite, about 10% from ion adsorption ores, 5% from monazite and the remaining from other sources such as xenotime, loparite, and brannerite (Gupta and Krishnamurth, 2005; Papangelakis and Moldoveanu, 2014).

In the beneficiation technologies industrially applied for placer deposits (mainly monazite and xenotime) the physical methods gravity concentration, magnetic and electric separation commonly are used for seperation of monazite and xenotime from other minerals, ilmentite, garnet, zircon, magnetite, rutile and light minerals quartz and mica etc., and flotation is also used for fine grained placer ores (Fig.1 to 4) ((Gupta and Krishnamurth, 2005).
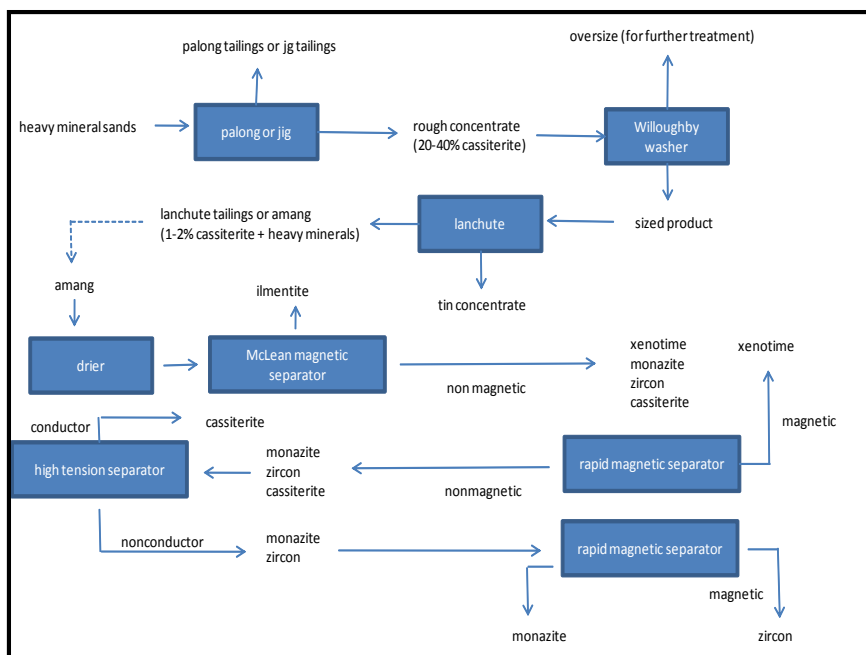
Fig.1 Physical beneficiation of cassiterite-bearing mineral sands of Southeast Asia
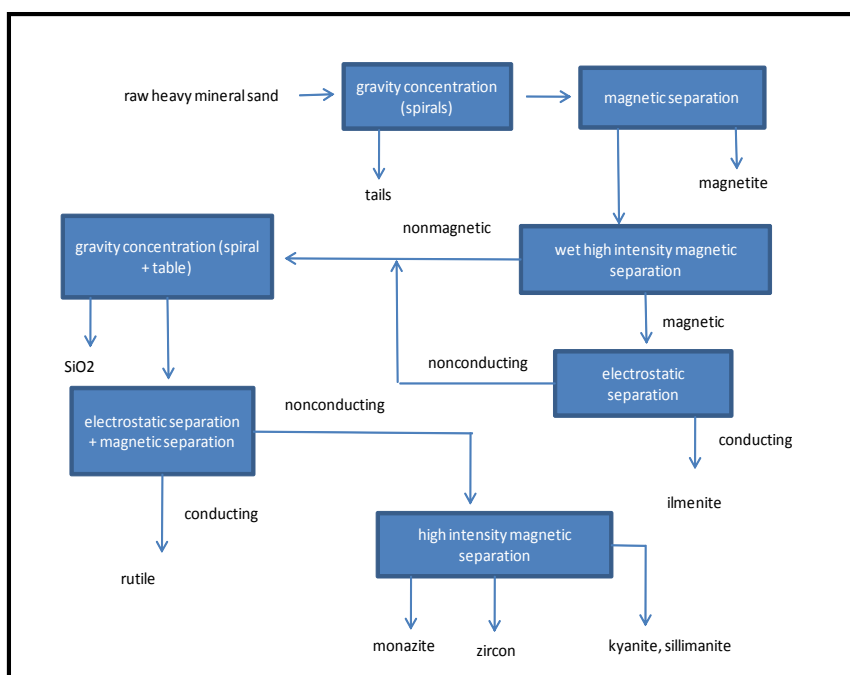


Fig.2 Beneficiation of coarse heavy mineral sand from Congolone, Mozambique
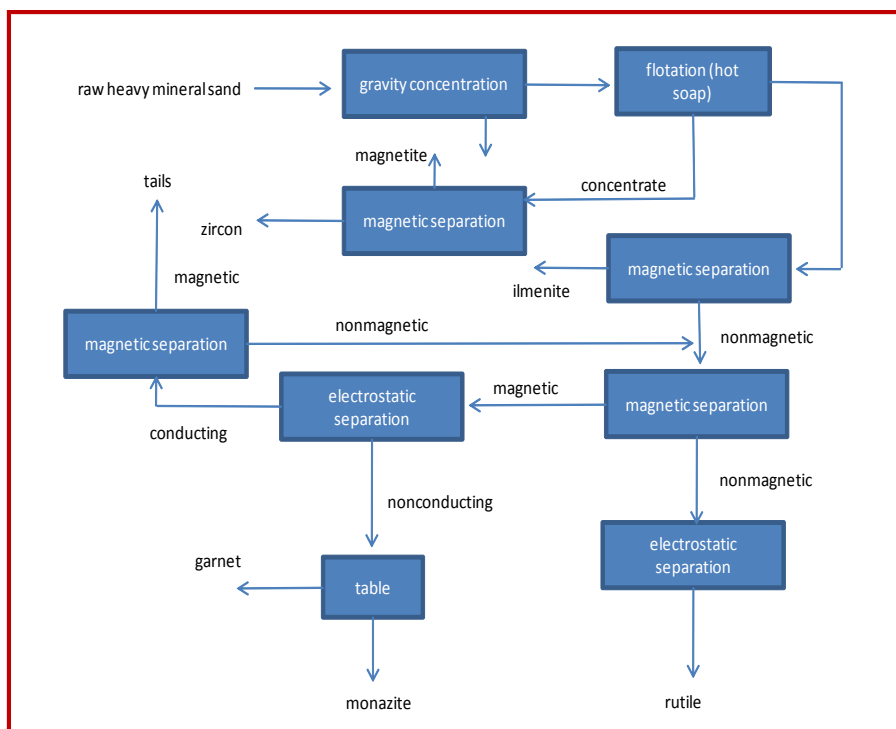
Fig.3 Beneficiation flowsheet at Zircon Rutile Ltd., Australia
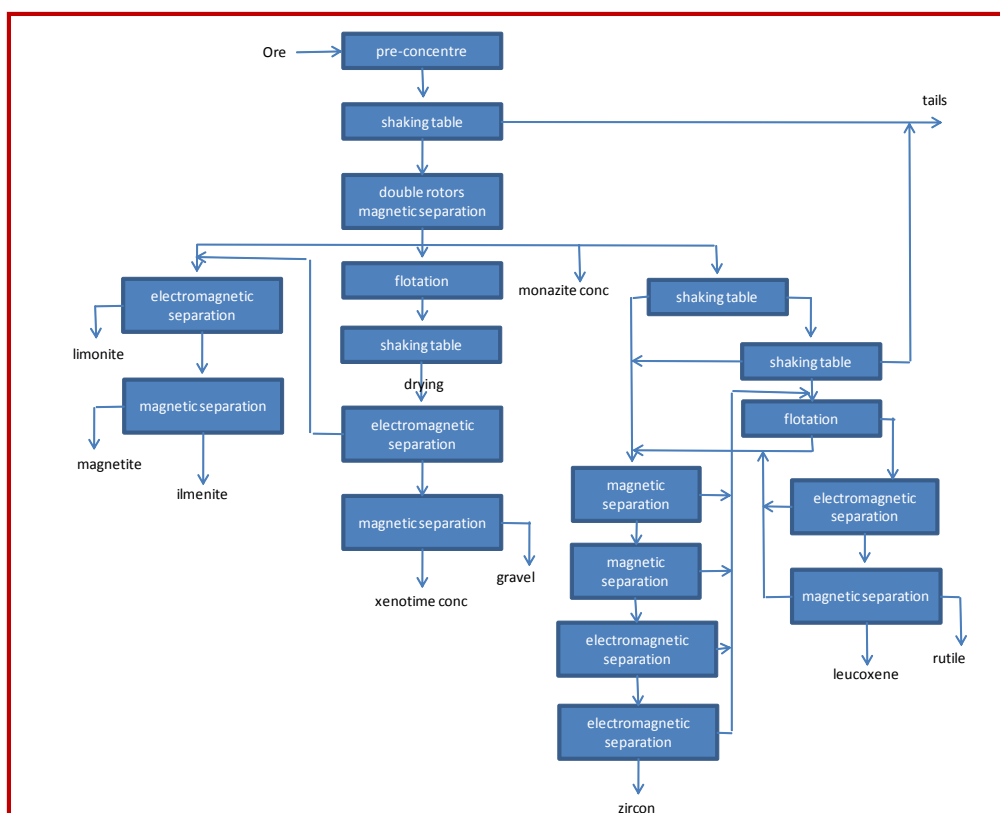


Fig.4 A xenotime separation process for a coastal placer deposit in South Eastern China

For hard rock deposits (mainly bastnäsite but also monazite) the developed beneficitaion flowsheets or the flowsheets successfully used in industrail plants are for the separation of bastnäsite and monazite from other minerals such as silicates and Fe-oxides etc., for example, the beneficiation technologies on Mountain Pass and Bayan Obo ores.

The Mountain Pass ore is a bastnäsite ore with average REO 7%. Flotation is used for the recovery of bastnäsite. Various collectors such as fatty acids (oleic), distilled tall oil (fatty and rosin acids) and hydroxamates (1988) have been used. High temperature 70-90 °C conditioning treatments are applied at high solids with reagents added at pH8.8 using soda ash and sodium fluosilicate as the depressant. The final flotation concentrate containing 60% REO is sent to leaching using 10% HCl to leach out lime. The concentrate containing 70% REO is produced. Calcination is also used to decompose the carbonate and obtain 90% grade bastnäsite concentrate (Gupta and Krishnamurth, 2005). The flowsheet is shown in Fig.5.
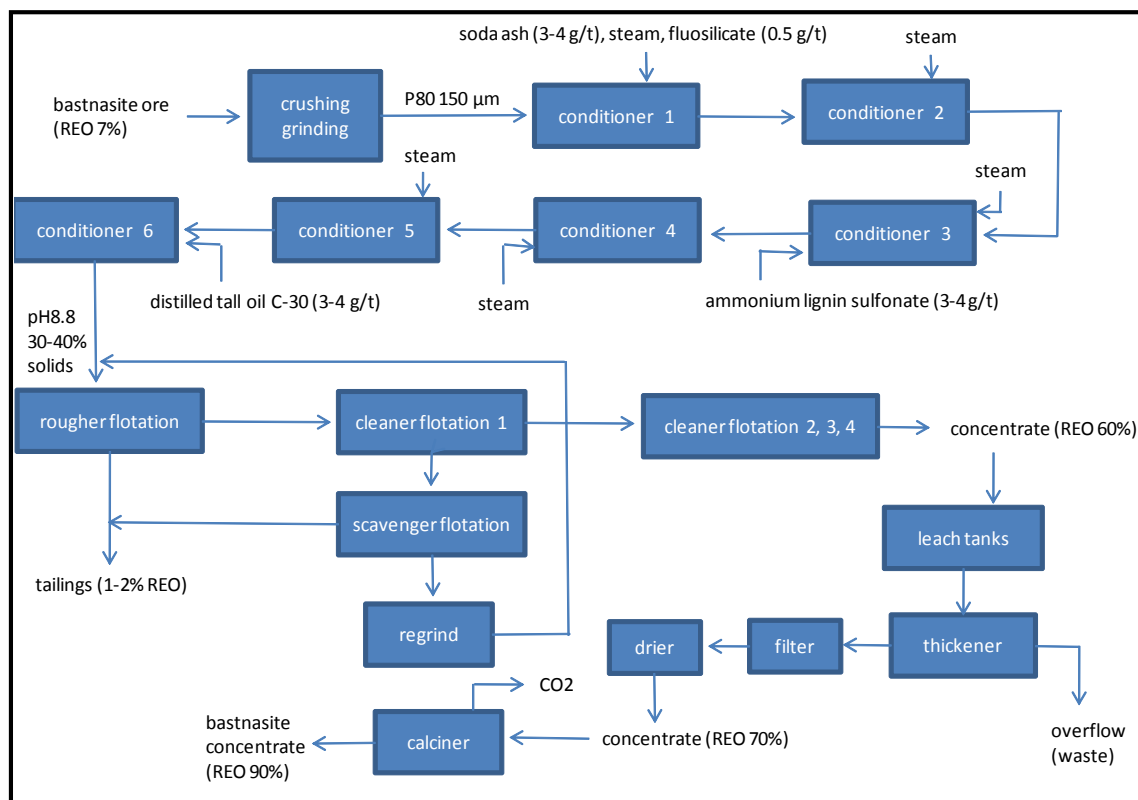


Fig.5 Flowsheet of Ore Beneficiation at Mountain Pass Mine

As shown in Fig.6 for the Bayan Obo REE-Nb-Fe ore, the principle RE minerals are bastnäsite and monazite in the ratio of 7:3 or 6:4. The flowsheet of low intensity magnetic separation (LIMS) – high intensity magnetic separation (HIMS) – flotation was considered the most successful one to be used in industrial plants. By LIMS magnetite is recovered and the tailings of LIMS is processed through HIMS rougher at the magnetic field strength of 1.4T to recover another Fe mineral hematite and most REE minerals. Hematite and REE minerals contained in the HIMS rougher concentrate are separated by HIMS cleaner at the magnetic field strength of 0.6T. Combined LIMS and HIMS concentrates reported to the Fe reverse flotation to get the final Fe concentrate and the HIMS cleaner tailings containing most REE minerals is processed by flotation to get REE

concentrates Flotation is performed at low alkaline condition (pH9) with the reagents naphthyl hydroxamic acid as the collector of RE minerals and sodium silicate as the depressant of silicates (Li and Yang, 2014).
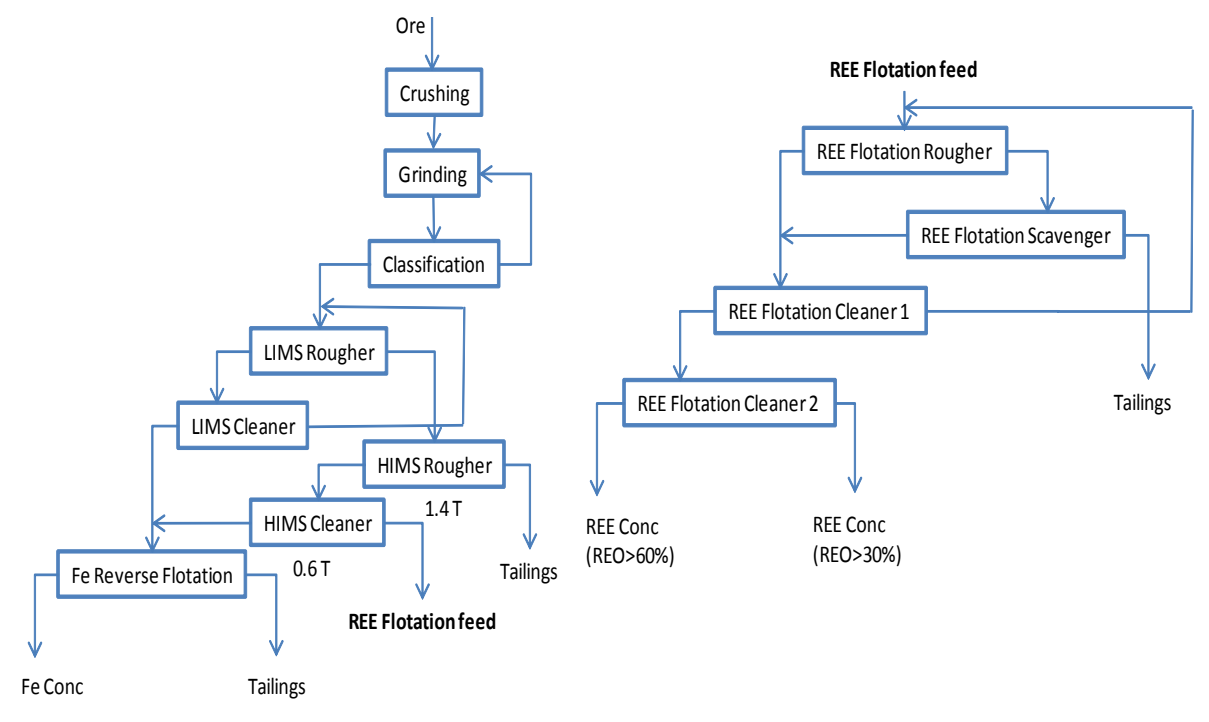


Fig.6 Beneficiation flowsheet of the Bayan Obo deposit ore

Direct leaching is used industrially for the extraction of REE from the ion adsorption ores in China which contain high heavy REE (Fig.7). The 80% –90% REE in the state of positive hydrated ions are adsorbed on the surface of clay minerals such as kaolinite, halloysite and illite at low-grade 0.05% to 0.5% REO. The electrolytes solutions of NaCl, $(NH4)2SO4$ or $NH4Cl$ are used to dissolve the adsorbed REE ions from the mineral surface by ion–exchange. Oxalic acid is used as the precipitant to get mix product of oxalic acid–rare earths which is further processed by roasting to get final rare earths product (>REO 92%) (Chi and Tian, 2007; Li and Yang 2014). Now China produces about $1×104$ t concentrate (REO >60%) from this ore annually.
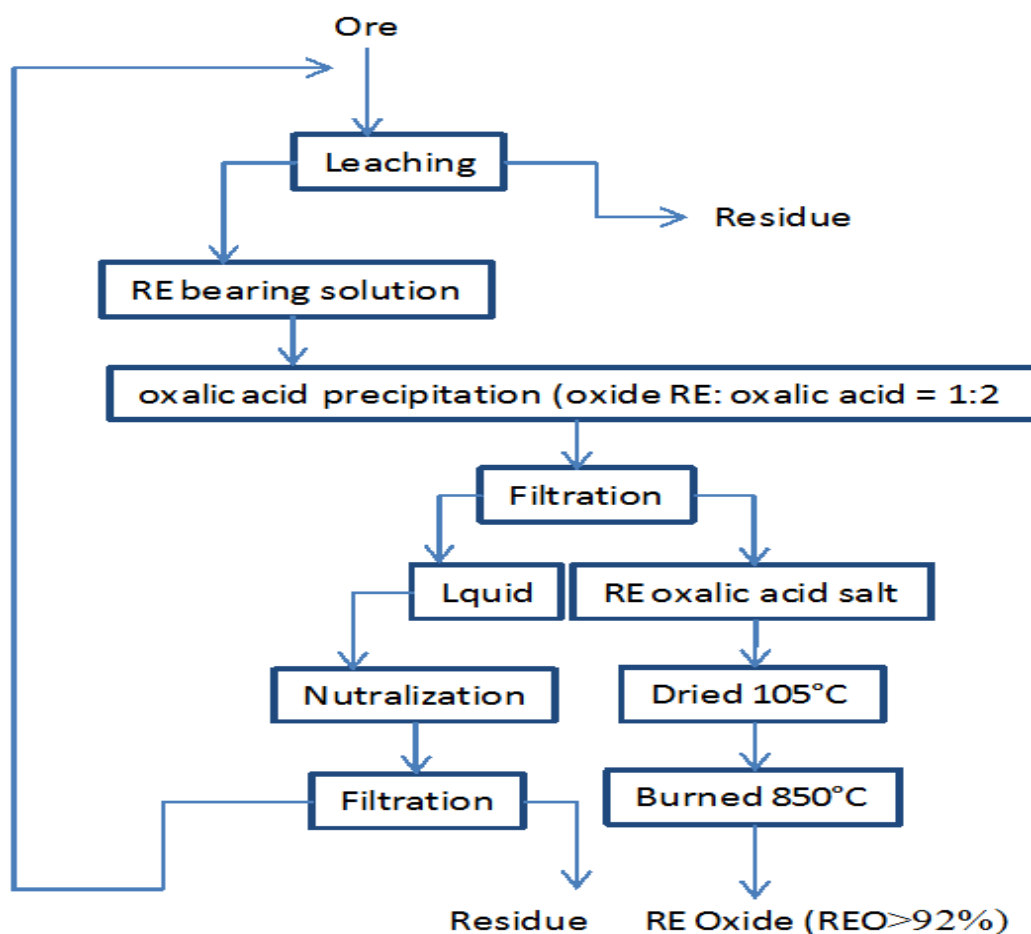
Fig.7 Extraction flowsheet of REE from the ion adsorption ores in China

Loparite is an oxide rare earth mineral similar to perovskite, found extensively in Russia's Kola Peninsula where almost 6500 tons of REO are extracted annually. This mineral occurs alongside gangue such as aegirine, feldspar, nepheline and ramsayite and is concentrated via a combination of gravity and magnetic separation techniques (Hedrick et al., 1997). Several other rare earth minerals (including eudialyte, apatite and synchysite (Y)) are extracted in this region.

## 22.2.2 METALLURGICAL EXTRACTION

Beneficiation concentrates of rare earths are usually leached with aqueous inorganic acids, such as HCl, H2SO4, and HNO3, or treated with NaOH for attacking the mineral. After filtration or counter current decantation (CCD), solvent extraction is used to separate individual rare earths or produce mixed rare earth solutions or compounds. Commercial extraction of rare earth metals has been carried out using different extractants viz. D2EHPA, HEHEHP, Cyanex 272, PC 88A, Versatic 10, TBP, Aliquat 336, etc. (Manis Kumar Jha et al., 2016; Feng Xie et al., 2014).

### 22.2.2.1     CHEMICAL TREATMENT

Bastnäsite

In order to reduce the acid consumption, bastnäsite concentrates are typically roasted to decompose the carbonate minerals before leaching with either hydrochloric or sulfuric acid.

The bastnesite concentrates from the Bayan Obo at Baotou China contain a small amount of monazite. The leaching process has been designated to be flexible and to accommodate different concentrates (Figure 8).

Rare earth concentrate (50% wt. REO)

↓

ROASTING ← Concentrated H2SO4

↓

Calcined concentrate          Off-gas

↓

LEACHING

↓

NEUTRALIZATION/PRECIPITATION/FILTRATION

↓

Leachate                      Residue

Solvent extraction          Precipitation with ammonium carbonate and
(separation individual REE)  dissolution with HCl to produce mixed REE
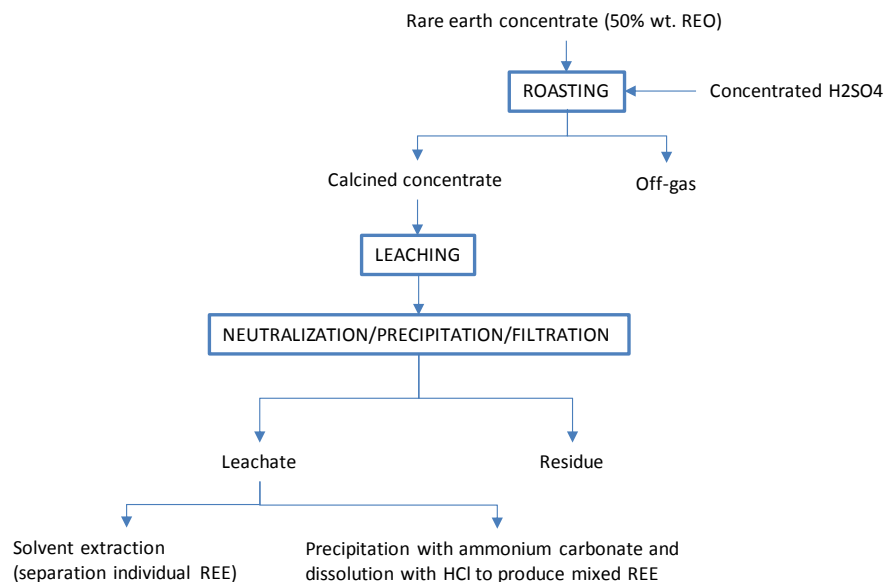
Fig. 8 Leaching process used for Baotou rare earth concentrates in China (Huang et al., 2006).

The process starts with roasting with concentrated sulfuric acid at >300 °C. The rare earth sulfates formed during this process are then leached with water, and excess acid is neutralized with magnesia and filtered. The leach solution then proceeds to solvent extraction, alternatively a mixed rare earth chloride (for electrolysis to misch metal) could be produced by precipitation with ammonium carbonate, followed by dissolution with HCl and crystallization.

Monazite

Monazite concentrates can be leached either by sulfuric acid or by sodium hydroxide at elevated temperature to decompose the orthophosphate lattice. The sodium hydroxide treatment is preferred in most commercial extraction plants because it better separates phosphate from the rare earth.

*Acid treatment*   The sulfuric acid method had been used extensively in the U.S. Depending on the acid/ore ratio, temperature and concentration, either Th or REE can be selectively solubilized or both totally solubilized. REE and Th are subsequently recovered from the solution. The sulfuric acid method is no longer in commercial use because no pure products are yielded.

*Alkali treatment*   Currently, sodium hydroxide wth a 70% solution is usually employed for leaching monazite at 140–150 °C for 2-4 h. The reactions during alkaline leaching are:

$REPO_4 + 3NaOH = RE(OH)_3 + Na_3PO_4$

$Th_3(PO_4)_4 + 12NaOH = 3Th(OH)_4 + 4Na_3PO_4$
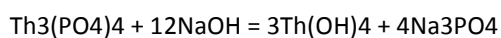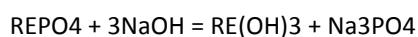
The residue containing rare earth metals and thorium hydroxide is treated in hot nitric acid and sulfuric acid, or hydrochloric acid to prepare REE solutions solvent extraction.

Prior to this process, proper grinding of monazite is essential to obtain high extraction about 98% even with relatively low grade ores (Manis Kumar Jha et al., 2016). Studies on the decomposition of an Australian monazite concentrate (48.6% REE, 6% thoria, 31% phosphate) pointed out that the extraction reached 98% only digesting fine ground (less than 45 micron) monazite concentrate in 80% w/v (NaOH: monazite weight ratio 1.5:1) at 140 °C for 3 h. Studies on Brazilian monazite have also confirmed tha necessity of fine grinding and high temperature (140-200°C) for effective decomposition (Gupta and Krishnamurthy, 2005).

Both "hydrothermal" and soda fusion methods were used to investigate the chemical treatment of a Taiwanese black monazite. In the hydrothermal process, ground monazite was cracked with 455 wt% of aqueous alkali solution at 170 °C and 5 atmospheres in an autoclave for 3 h. As an alternative unground monazite were fed into fused caustic soda at 400 °C in an open cylindrical stainless steel tank and reacted the mass for 2.5 h with low speed agitation. In each of these operations, 90% of the REE conained in the monazite was recovered (Gupta and Krishnamurthy, 2005).

A process involving high temperature reaction of monazite with calcium chloride and calcium carbonate has been suggested by Merritt (1990). In this process monazite is decomposed by reacting it with calcium chloride and calcium carbonate in an environment that is both reducing and sulfidizing at temperature 980-1190 °C. The products formed are REE oxysulfides, oxychlorides, a thorium rich oxide solid solution, and a calcium chlorophosphate (chloropatite). From the product, the REE are removed by leaching with 3% HCl. Filtration is used to separate the each liquor from the gangue minerals that remain as the residue. The thorium rich oxide residue is resistant to acid attack and is suitable for disposal by burial (Gupta and Krishnamurthy, 2005).

Xenotime

Either sulfuric acid leaching or alkali leaching methods are used for the extraction of rare earth metals from xenotime (Gupta and Krishnamurthy, 1992). Different authors reported different methods using sulfuric and nitric acid, alkaline solution, water leaching after roasting with ammonium salt to leach out rare earth metals directly or after pre-treatment to improve dissolution behavior of the constituents. The process options for treating xenetime concentrate are shown in Figure 9.

Xenotime Conc

```
digestion              roasting (Na2CO3)         fusion
(H2SO4 93%)            900°C                     400°C
190-250°C

   │                         │                      │
leaching (H2O)          leaching (H2O)          extraction
                                                (H2O, NH4Cl)
   │                         │                      │
filtration              filtration              dissolution
   │                         │                      │
RE sulphate             dissolution             RE chloride
                             │
                        RE nitrate
```
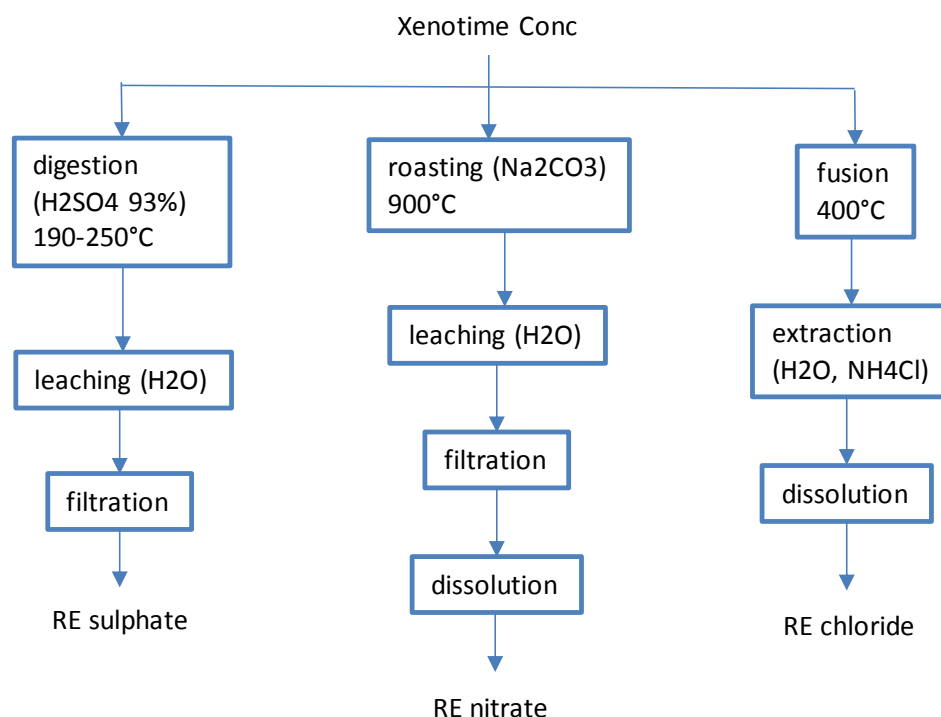
Fig.9   Chemical processing of xenotime

The acid process for xenetime breakdown involves attacking with concentrated (93%) sulfuric acid. The rare earth phosphates are converted to water soluble sulfates by leaching xenotime concentrate in $H_2SO_4$ at 250-300 °C for 1-2 h. Such leaching was uneconomical for concentrates containing less than 10% xenotime. These are treated by wetting the solids with sufficient acid and heating the mass at 300 °C followed by water leaching. About 80-90% of the rare earths are solubilized. The recovery of rare earths by the processes such as double sulfate precipitation is not possible because yttrium and the heavy rare earth sulfates are quite soluble. The sulfate solution is directly taken for separation. In the alternative process, the fine ground xenotime is treated by fusing it with molten caustic soda at 400 °C or by mixing it with sodium carbonate and roasting at 900 °C for several hours. After leaching out the phophates, the hydroxide residue is dissolved in a minimum amount of hydrochloric acid and filtered from impurities such as silica, cassiterite, etc. The rare earths are recovered by precipitation as oxalates.

The process used in the plant of the Malaysian Rare Earth Corporation (MAREC) located at Bukit Merah in Perak state, Malysia, for the production of yttrium oxide concentrate from xenotime is outlined (Gupta and Krishnamurthy, 2005; Sulaiman, 1991) in Figure 10.

```
xenotime → milling → roasting → digestion → slurry → leaching
                                 (conc. H2SO4)        (cold water)

Calcination ← yttrium oxalate ← precipitation ← filtration
                                 (oxalic acid)
   │
yttrium oxide
```
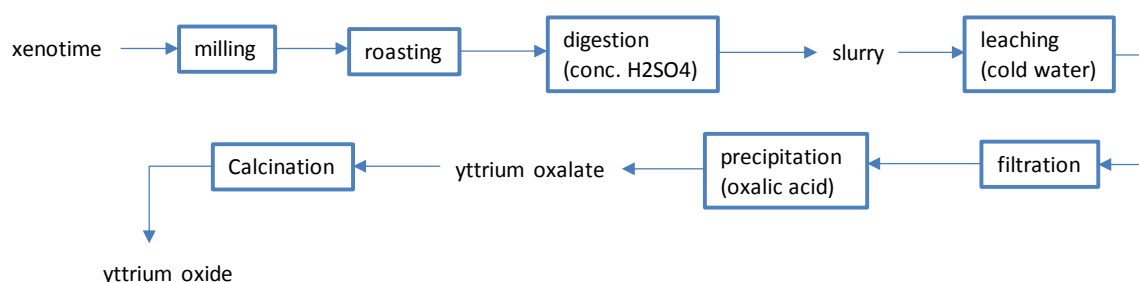
Fig.10  Xenotime processing at Malaysian Rare Earth Corporation

The xenotime is first milled to a required particle size and then roasted in a furnace. These operations ensure that good recovery is obtained in the next stage, which is sulfuric acid digestion of the roasted material. By sulfuric acid digestion, YPO4 in the xenotime is converted to the water soluble sulfate. Cold water is used as the leachant for better recovery. Oxalic acid is added to the yttrium sulfate solution to precipitate yttrium oxalate. The final stage is the calcination of yttrium oxalate to the oxide. The plant has a capacity to produce 200 t of yttrium concentrate (60% Y2O3) per year.

The ion-adsorption type rare earth ores

In the ion-adsorption type rare earth ores the 80% −90% of rare earths in the state of positive hydrated ions are adsorbed on the surface of clay minerals such as kaolinite, halloysite and illite. The ore is relatively low-grade, generally only REO 0.05% to 0.5 wt%, with high heavy rare earths (Chi and Tian 2007, 2008). Because rare earths in the ore mainly occur in the state of hydrated ions adsorbing on the surface of clay minerals they can't be effectively concentrated by conventionally physical methods. The adsorbed rare earths ions are usually dissolved in the electrolytes solutions of NaCl, (NH4)2SO4 and NH4Cl by ion–exchange (Li and Yang, 2015). The leach solution will usually contain dissolved impurities such as iron, which are removed by precipitation before proceeding to solvent extraction to separate the rare earths (Feng Xie et al., 2014).

## 22.2.2.2    SEPARATION OF REE

Depending on the process, some primary REE producers may choose to sell intermediate, mixed products, or perform different downstream separations to produce individual REE salts or oxides.
Separation processes based on ion-exchange and solvent extraction techniques have thus been developed to produce high purity single rare earth solutions or compounds. Before the advent of industrial scale solvent extraction in the 1960s, ion exchange technology was the only practical way to separate the rare earths in large quantities. Currently, ion exchange is only used to obtain small quantities of high purity rare earth product for electronics or analytical applications. Solvent extraction is generally accepted as the most appropriate commercial technology for separating rare earths (Feng Xie et al., 2014).

## SOLVENT EXTRACTION

Solvent extraction is an important technique that is usually employed to separate and extract individual metals or to get their mixed solutions and compounds. To develop feasible and eco-friendly processes, R&D studies are being conducted for rare earth extraction from leached solutions using various solvents viz., anionic, cationic and solvating depending on material and media. The commercial extraction of rare earth metals from different leached solutions (chloride, nitrate, thiocyanate, etc.) using different cationic, anionic and solvating extractants viz. D2EHPA, Cyanex 272, PC 88A, Versatic 10, TBP, Aliquat 336, etc (Manis Kumar Jha et al., 2016).

Their commercial value depends upon the purity and quality of the compound which is based on effective separation of the individual metals. Thus, for pure rare earth recovery from leached solutions, difference in their basicity and formation of species in the aqueous phase is employed for their selective oxidation/reduction, fractional precipitation, crystallization, ion exchange and SX processes. In SX process, rare earth separation and purification are made from the acidic/alkaline leached solution containing impurities such as Ca2+, Fe3+, A13+, and Pb2+, which affects the quality of the products formed and can be removed using precipitation process. Different extractants, naphthenic acid, di-(2-ethyl-hexyl) phosphoric acid (D2EHPA), 2-ethylhexyl phosphonic
acid mono 2-ethylhexyl ester (PC 88A, Ionquest 801), versatic acid, trialkyl-methyl ammonium chloride (Aliquat 336), bis (2,4,4- trimethylpentyl) phosphinic acid (Cyanex 272), tributyl phosphate (TBP), etc. are used as extractants for rare earth extraction in various industries (Gupta and Krishnamurthy, 2005; Thakur, 2000a). D2EHPA is the most widely studied extractant for rare earth separation from nitrate, sulfate, chloride and

perchlorate solutions. Saponified PC 88A has been reported for their separation from chloride solutions while tributyl phosphate (TBP), a solvating extractant that extracts their nitrates from the aqueous solutions. Anionic complex from the aqueous solution is extracted usingamine based extractants. Selective separation of some rare earth metals (Eu and Ce) are made based on their valence state in aqueous solution. The extractant, long chain quaternary ammoniumsalts has been used on commercial scale for the separation of high purity yttrium (Y) (Manis Kumar Jha et al., 2016).

The separation of trivalent lanthanides as a group from actinides as well as individual lanthanides fromeach other is a formidable challenge in the field of separation science. The lanthanides are usually separated using multistage extractions in counter-current mode in mixer settlers which are tedious and time consuming. Therefore, the development of new extraction systems for separation of lanthanides as a group or from one another using ion-specific compounds/solvents has also been reported. Several stages of mixer-settlers are employed for their separation on industrial scale. For leached solutions containing lowconcentration of rare earth metals, different ion exchange cationic or anionic resins are employed depending on the constituent of the aqueous solution using batch or continuousmode in column. The purified solution obtained after separation could be further processed to produce the value added products in the form of salt for industrial application (Manis Kumar Jha et al., 2016).

Different organic solvents used for the extraction of rare earth metals are shown in Table 5 and the results for extraction of rare earth metals using various extractants from different solutions are shown in Table 6.

Table 5 Different organic solvents used for the extraction of rare earth metals.

| Extractants | Chemical Name | Producing company |
|---|---|---|
| Cyanex 272 | Di-2,4,4,-trimethylpentyl phosphinic acid | Cytec Limited, Canada |
| D2EHPA | Di-2-ethylhexyl phosphoric acid | Luoyang Aoda Chemical Ltd., China |
| PC 88A | 2-Ethylhexyl phosphonic acid mono 2-ethylhexyl ester | Daihachi Chemical Industry, Japan |
| TBP | Tri-n-butyl phosphate | Luoyang Aoda Chemical Ltd., China |
| Kelex 100 | 7-(4-Ethyl-1-methyloctyl)-8-hydroxyquinoline | Sherex Chemicals, USA |
| LIX 84 | 2-Hydroxy-5-nonylacetophenoneoxime | BASF Corporation, USA |
| Versatic 10 | Alkyl monocarboxylic acids | BASF Corporation, USA |

| Aliquat 336 | Tri-octyl methylammonium chloride | BASF Corporation, USA |
|---|---|---|

Table 6 Results for extraction of rare earth metals using various extractants from different solutions.

| Extractant | Aqueous feed | Salient features | References |
|---|---|---|---|
| 2,6-Bis(5,6-dipropyl-1,2,4-triazin-3-yl) pyridine (n-Pr-BTP)<br><br>in n-dodecane/1-octonol | A mixture of Am3+ and Eu3+ in<br><br>nitrate solution | Almost 85% Am3+ and 6% Eu3+ extracted in 6 h with 0.03<br><br>M n-Pr-BTP in n-dodecane/1-octanol (7:3) diluent<br><br>mixture from 1 M NaNO3 at pH 2. | Bhattacharyya<br><br>et al. (2011) |
| 4-Methyl-2-pentanone (MIBK) containing<br><br>3-phenyl-4-acetyl-5-isoxazolone (HPAI),<br><br>1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP) and<br><br>thenoyltrifluoroacetone (HTTA) | Aqueous solution containing<br><br>La(III), Ce(III), Eu(III), Th(IV) and<br><br>U(VI) | Extraction into MIBK containing HPAI found to be better<br><br>extractant on comparing the extraction of the metals<br><br>containing HPMBP and HTTA. | Jyothi and Rao<br><br>(1989) |
| HPBI (3-phenyl-4-benzoyl-5-isoxazolone) in chloroform | La(III), Ce(III), Eu(III), Th(IV) and<br><br>U(VI) in HCl | Extraction found to increase with pH and became almost<br><br>quantitative near the pH at which the metal ion<br><br>hydrolyses. Plots of log Kd vs. pH at constant ligand<br><br>concentration gave straight lines with slopes of around<br><br>two for U, three for La, Ce and Eu, and four for Th. | Jyothi and Rao<br><br>(1990) |

| | | | |
|---|---|---|---|
| 1-Phenyl-3-methyl-4-trifluoroacetyl pyrazolone-5 (HPMTFP) mixed with dicyclohexano-18-crown-6 (DCH18C6) and monobenzo-15-crown-5 (B15C5) in chloroform | Trivalent metals (Am, Cm, Cf and Eu) in 0.1 M NaClO4 | With DCH18C6 the synergistic species extracted are M(PMTFP)3·(HPMTFP)(DCH18C6), (PMTFP)3·(DCH18C6), whereas with (B15C5) species are M(PMTFP)3·n(B15C5), n being 1 or 2 for all these metal ions. | Mathur and Khopkar (1988) |
| PC 88A in paraffinic kerosene | Dy and Tb from rare earths chloride solution from monazite | PC 88A extracted Dy and Tb from chloride solution. Dy and Tb were recovered with a purity of 97% and 83% respectively. | Mishra et al. (2000) |
| Cyanex 923 (TRPO) in xylene | Trivalent lanthanides (La, Nd, Eu, Tb, Ho, Tm, Lu) and yttrium (Y) in thiocyanate and nitrate solutions | Metal ions extracted from thiocyanate solution as $M(SCN)_3 \cdot nTRPO$; [n=3 and 4 for the lighter and heavier lanthanides respectively]. In nitrate solutions, metal ions are extracted as $M(NO_3)_3 \cdot 3TRPO$. | Reddy et al. (1998) |
| Mixtures of Cyanex 301 and Cyanex 923 (TRPO) in xylene | Trivalent rare earths in nitrate solutions | Trivalent rare earth metal ions extracted as $MX_3 \cdot 3HX$ | Reddy et al. (1999) |

| | | with Cyanex 301. In presence of Cyanex 923, La and Nd<br><br>are extracted as MX2·NO3·TRPO whereas Eu, Y and other<br><br>HREMs extracted as MX3·HX·2TRPO. | |
|---|---|---|---|
| 4Sebacoylbis(1-phenyl-3-methyl-5-pyrazolone) (H2SP) and<br><br>4-dodecandioylbis(1-phenyl-3-methyl-5-pyrazolone)<br><br>(H2DdP) in chloroform | Actinides [Th(IV), U(VI)] and<br><br>Ln(III) (Nd, Eu, Lu) in nitrate<br><br>solutions | Metal ions get extracted as Th(SP)2, Th(DdP)2,<br><br>UO2(HSP)2, UO2(HDdP)2, Ln(SP)(HSP) and<br><br>Ln(DdP)(HDdP) with H2SP or H2DdP. Th(IV) selectively<br><br>separated from U(VI) and Ln(III) from 0.2 mol/L nitric<br><br>acid using 4-acylbis (1-phenyl-3-methyl- 5-pyrazolones). | Reddy et al.<br><br>(2000) |
| 1-Phenyl-3-methyl-4-benzoly-5-pyrazolone (HPMBP) in<br><br>chloroform<br><br>−. | All RE ions (except Pm) and Y in<br><br>0.1 M (Na, H)+ ClO4 | Formation of Ln(PMBP)3, two-phase stability constants<br><br>(logβ3·PLn(PMBP)3), pH for 50% extraction of metal<br><br>chelates (pH50) and separation factors (S) between the<br><br>adjacent elements have been evaluated using 5 × 102− M  HPMBP. | Roy and Nag<br><br>(1978) |

| | | | |
|---|---|---|---|
| A mixture of phenyl-3-methyl-4-benzoyl-pyrazalone-5 (HPMBP) and bis-(2-ethylhexyl)sulphoxide (B2EHSO) or octyl(phenyl)-N,N-diisobutylcarbamoyl methylphosphine oxide (CMPO) in xylene. | Metals (M = La, Eu, Lu and Am) in chloroacetate | HPMBP extracted metal ions as M(PMBP)3·HPMBP. With B2EHSO as a neutral donor, the synergistic adduct species were M(PMBP)3·B2EHSO and M(PMBP)3·2B2EHSO, whereas with CMPO as a neutral donor the only complex extracted into the organic phase is M(PMBP)3·CMPO | Santhi et al. (1994) |
| TOPS 99, PC-88A and Cyanex 272 in kerosene as diluent | Mixture of seven HREEs (Tb, Dy, Ho, Y, Er, Yb, Lu) and four LREEs (La, Ce, Pr, Nd) in phosphoric acid | Extraction efficiency of extractants towards lanthanides from H3PO4 medium decreases in the series: TOPS 99 N PC 88A N Cyanex 272. | Radhika et al. (2010) |
| TOPS 99 in kerosene | LREEs La, Ce, Pr, Nd, and seven HREEs like Tb, Dy, Y, Ho, Er, Yb and Lu) in phosphoric acid solutions | The studies showed the separation of a mixture of rare earth metals into three concentrates, two heavy rare earth fractions (Yb + Lu and Tb, Dy, Ho, Y, Er) and one light raere earth fraction from 3 M acid using 1 M TOPS 99. | Radhika et al. (2011) |

Ion exchange and precipitation

Before 1960, ion exchange method was the only way to separate rare earth metals but currently it is used only to extract small quantities of highly purified rare earth products (Xie et al., 2014). During ion exchange process, different ion exchange cationic or anionic resins are employed depending on the constituent of the aqueous solution using batch or continuousmode in column to extract rare earths from leached solutions with low rare earth concentration. The purified solution obtained after separation could be further processed to produce the value added products in the form of salt for industrial application. Application of ion exchange resins eliminates the requirement for a costly solid/liquid separation unit as in case of SX processes (Padayachee et al., 1996).

The chemical as well as spectrochemical analyses showed a natural fractionation of rare earth metals and the considerable variation in their proportion could show progressive differentiation. The study of fractional precipitation of adjacent pairs of rare earth metals provides information regarding their individual distribution and also, the possible mode of formation, and order of crystallization and deposition of the minerals. Solubility and fractional precipitation studies of the lanthanides in such systems as the oxalate, bromate, and sulfate are reported, indicating different orders of preferential precipitations. These studies were undertaken primarily for their possible application to the development of techniques for separating and purifying some of the lanthanides. Studies have been carried out by various researchers to extract rare earth metals using different types of ion exchange resins such as Tulsion CH-96, Tulsion CH-93, T-PAR, and IR-120P or by the process of precipitation using reagents viz. sodiumsulfate, oxalic acid, ammonia, etc. and the detail study is presented in Table 7 (Manis Kumar Jha et al.,2016).

Table 7 Studies on extraction of rare earth metals using different types of ion exchange resins

| Resin used | Salient features | References |
|---|---|---|
| Tulsion CH-96 and T-PAR | Solid-phase extraction of heavy rare-earths like Tb, Dy, Ho, Y, Er, Yb and Lu from phosphoric acid using Tulsion CH-96 and T-PAR resin has been reported. | Kumar et al. (2010) |
| IR-120P (cation-exchange polymeric resin) | Recovery of Y and rare earths using electroelution of a cation-exchange polymeric resin IR-120P Rohm & Haas-USA from chloride medium is reported. | Pinto and Martins (2001) |
| N-methylimidazolium functionalized anion exchange resin | N-methylimidazolium functionalized anion exchange resin was used for adsorption of Ce(IV) from nitric acid medium by reducing it to Ce(III). | Zhu and Chen (2011) |
| Tulsion CH- | 93 Solid–liquid extraction of Gd from phosphoric acid medium using amino phosphonic acid resin, Tulsion CH-93 is reported. The log D vs. equilibrium pH plot gave straight line with a slope of 1.8. The loading capacity of Tulsion CH-93 for Gd was 10.6 mg/g. | Radhika et al. (2012) |

| Dowex I-X8 anion-exchange resin | The distribution coefficients on Dowex I-X8 was determined for all rare earths at different proportions of nitric acid and acetone which is found to be sufficient for the separation of rare earths by ion-exchange chromatography. | Alstad and Brunfelt (1967) |
|---|---|---|
| D113-III resin | The adsorption and desorption behaviors of Er(III) ion using resin D113-III were investigated. The loading of Er(III) ion onto D113-III increased on increasing the initial concentration. | Xiong et al. (2009) |
| D72 (acid ion exchange resin) | The loading of Pr (III) ions was dependent on pH and adsorption kinetics of Pr (III) ions onto D72 resin followed pseudo-second-order model. The maximum adsorption capacity of D72 for Pr (III) was evaluated to be 294 mg g−1 for the Langmuir model at 298 K. | Xiong et al. (2012) |
| D151 resin | The adsorption and desorption behaviors of Ce(III) on D151 resin was achieved at pH 6.50 in HAc–NaAc medium. The maximum loading capacity of Ce(III) was 392 mg/g resin at 298 K. | Yao (2010) |
| Bio-Rad AG 50W-X2 cation-exchange resin | A new method for determining the stability constants for the mono- and difluoro-complexes of Y and rare earths, using a cation-exchange resin Bio-Rad AG 50W-X2 has been reported. | Schijf and Byrne (1999) |
| TODGA resin | A two-stage method to separate Lu and Hf from silicate rock and mineral samples digested by flux melting or HF–HNO3 dissolution using TODGA resin from Eichrom Industries is presented. | Connelly et al. (2006) |

| | | |
|---|---|---|
| Amberlite XAD-4 | The pre-concentration and separation of La(III), Nd(III) and Sm(III) in synthetic solution was achieved using Amberlite XAD-4 with monoaza dibenzo 18-crown-6 ether. The adsorbed rare earth elements were eluted by 2 M HCl. | Dave et al. (2010) |
| D152 resin | The sorption of rare earth ions from HAC–NaAC buffer solution using D152 resin containing –COOH function groups at 298 K are presented. | Xiong et al. (2008) |
| XAD-4 (crosslinked polystyrene resin) | A new chelating agent bis-2[(O-carbomethoxy)phenoxy]ethylamine has been synthesized using a facile microwave induced process. The ligand was appended on to XAD-4 resin and adsorption properties of La(III), Nd(III) and Sm(III) towards this resin were studied. The selectivity sequences of the resin for these metals were in agreement with their stability constants. | Kaur and Agrawal (2005) |
| Tertiary pyridine resin | The novel separation method of rare earths using tertiary pyridine type resin with methanol and nitric acid mixed solution was developed. The adsorption and separation behaviors of rare earths were investigated and found that it can be well separated mutually. | Suzuki et al. (2006). |
| Precipitation process | | |
| Reagent used | Salient features | References |
| Sodium sulfate | A mixture of rare earths double sulfate was produced at 50 °C using 1.25 times the stoichiometric amount of Na2SO4. The total rare earths double sulfate | Kul et al. (2008) |

| | content was N90% together with minor amount of other impurities. | |
|---|---|---|
| Oxalic acid | Leach liquor obtained from weathered black earth contains rare earth metals along with other impurities. Oxalic acid was used to precipitates them forming rare earths oxalates, which are further roasted at 900 °C for 1.5 h to form rare earth oxides. | Chi et al. (2000) |
| Hydroxide–oxalate mixture | The filtrate obtained by leaching the roasted pre-concentrate of bastnasite with a dissolution percentage of 89% for total rare earths was separated from the residue.93.6% of total rare earths present were precipitated using hydroxide-oxalate mixture with its subsequent ignition to oxides at 900 °C for 2 h. | Yorukoglu et al. (2003) |
| Ammonium hydroxide | Ammonium hydroxide was used to precipitate lanthanum as lanthanum hydroxide at pH ranging from 7.9 to 9.6. Precipitation was made for three times which results in recovery of 96% lanthanum oxide. | Soe et al. (2008) |
| Ammonia | Lanthanum hydroxide and oxide were prepared by the precipitation method at room temperature. Lanthanum nitrate was dissolved in water and 2 M ammonia was added drop wise to precipitate lanthanum until pH ~ 10 was reached. | Kim et al. (2008) |
| Sodium hydroxide, ammonium hydroxide and potassium hydroxide | Double salt of neodymium is formed using sodium hydroxide, ammonium hydroxide and potassium hydroxide, which is further leached with HF to form neodymium fluoride. | Lyman and Palmer (1993) |
| Sodium hydroxide | A total recovery of 99% rare earths was obtained after selective | Innocenzi and Vegliò (2012). |

| | precipitation with sodium hydroxide at pH less than 2 after leaching the spent NiMH batteries by sequential sulfuric acid. A precipitate composed of lanthanum and cerium sulfates are produced. | |
|---|---|---|

## 22.3 TECHNICAL INNOVATIONS IN CRMS PRODUCTIONS FROM PRIMARY RESOURCES

### 22.3.1 MINERAL PROCESSING

There are only three major REE bearing minerals that are currently exploited commercially, bastnäsite and monazite in carbonatite deposits (Bayan Obo, Mountain Pass etc.) and monazite and xenotime in sand beach placer deposits, excluding ion-adsorbed clays, which currently undergo little or no beneficiation. In recent years, studies were conducted on beneficiation of other REE minerals such as steenstrupine from the Kvanefjeld deposit in Greenland by flotation, and eudialyte from the Norra Kärr deposit in Sweden and the Kringlerne deposit in Greenland by high intensity magnetic separation in the project EURARE (Yang and Krebs, 2016). Meanwhile, beneficiations of some complex REE ores and vein-type apatite REE ores were also investigated (Yang eta al., 2015, 2016).

In addition to the processing of beach sands, gravity separation, (shaking tables, spiral concentrators, and conical separators) is used in combination with froth flotation at many rare earth mineral processing operations throughout China (Jordens et al., 2013). An example of this is at Bayan Obo, where gravity separation has been employed between the rougher and cleaner flotation circuits to efficiently separate monazite and bastnäsite from the iron-bearing and silicate gangue material. In Maoniuping Sichuan, the China's second largest REE mine, magnetic separation and gravity separation were combined successfully to beneficiate a bastnäsite ore without using flotation.

Outside of China, lab-scale gravity separations have been successfully completed on Turkish and Australian deposits with very fine-grained mineralizations (Jordens et al., 2013). This was dealt with by either modifying the grinding steps to prevent excess fine generation or by employing a Multi- Gravity Separator, specifically designed to recover ultrafine particles via gravity separation. The modified grinding procedure employed an attrition scrubbing step prior to further grinding, while reducing the slimes loss to the -5 µm size fraction by an average of 7.8% (Jordens et al., 2013).

Common collectors used for bastnäsite flotation include variations of hydroxamates, fatty acids, dicarboxylic acids and organic phosphoric acids (Jordens et al., 2013; Jun et al., 2003). Typical depressants used in these situations include sodium silicate, sodium hexafluorosilicate, lignin sulfonate and sodium carbonate (Jordens et al., 2013).

Fatty acids have traditionally been the collector of choice in bastnäsite flotation due to their widespread availability and use in mineral flotation in general. However, they have been shown to be unselective for bastnäsite flotation comparing to hydroxamates (Bulatovic, 2007, 2010; Jianzhong et al., 2007) because the stable chelates with rare earth cations present on the mineral surface were formed using hydroxamates (Pavez

et al., 1996). Hydroxamic acids may exist two different forms, hydroxyamide or hydroxyoxime, but only the hydroxyamide form is able to form chelates with metal cations (Pradip and Fuerstenau, 1983). An additional benefit of the hydroxamic acids is that they are believed to interact with rare earth cations in solution to form hydroxylated rare earth ions, which then adsorb onto the mineral surface, acting as additional activation sites (Cheng et al., 1993). The enhanced selectivity of a hydroxamic acid (alkyl hydroxamate) in comparison to fatty acids (tall oil) at Mountain Pass has been explained by the fact that alkyl hydroxamate is more likely to form chelates with the rare earth ions in bastnäsite than the calcium and barium ions present on the mineral surfaces of calcite and barite (Jianzhong et al., 2007; Pavez et al., 1996; Pradip and Fuerstenau, 1983). The effectiveness of hydroxamic acids at the Bayan Obo mine has been shown to be affected by water hardness and decreasing pH, as $Ca^{2+}$ and $Mg^{2+}$ ions can consume large amounts of the collector, and excess hydrogen ions prevent the formation of the chelated compounds (Fangji et al., 1989).

The influence of temperature is, however, more complex in flotation since various other phenomena at the solid/liquid, solid/gas and liquid/gas interfaces are all affected simultaneously by temperature. It is very clearly established (Pradip, 1981 ) that temperature is the key to bastnaesite flotation. Some of the possible factors responsible for selectivity in flotation of Mountain Pass ore are discussed (Pradip and Fuerstenau, 1991). One effect of heating the pulp is perhaps to clean the surface of the various minerals and thus enhance the selective adsorption of reagent. Pradip and Fuerstenau (1991) compared the results of floating the ore with fatty acid collector and lignin sulfonate depressant under three conditions: ( 1 ) room temperature flotation; (2) flotation at room temperature after boiling the pulp without reagents followed by the addition of reagents at room temperature; and (3) the normal practice of conditioning and floating at high temperatures. The results very conclusively demonstrate that conditioning of the ore alone at high temperature does not affect the flotation. The results indicated that though lignin sulfonate functions as a selective depressant for barite, it does not become significantly more selective at higher temperatures. This then leaves the only possibility that it is really the selective adsorption of fatty acid collectors (alternatively, even more selective hydroxamate collectors ) which contributes to the selective separation of bastnaesite at elevated temperatures.

Pradip and Fuerstenau (1991) investigated the effect of conditioning temperature for both collector systems, (fatty acids and hydroxamate) on the flotation of Mountain Pass ore. The auxiliary reagents namely lignin sulfonate and soda ash were also added similar to the plant practice. The results seem to suggest that with fatty acids flotation, optimum temperatures may be around 70°-75 °C only rather than boiling temperatures. There is even a slight drop in concentrate grade observed during rougher flotation above 75 °C. With hydroxamate collectors also, the temperature has been observed to play a beneficial role on the recovery as well as the grade of bastnaesite concentrate. It was recognized that hydroxamates are not only more selective than fatty acids at room temperature but remain so even at elevated temperatures.

The Kvanefjeld deposit located in Greenland is claimed to be the world's second-largest deposit of rare-earth oxides, and the sixth-largest deposit of uranium (Bennet, 2010). The main REE mineral is steenstrupine, a sodium- lanthanide phospho-silicate. As early as in 1966 as part of the exploitation work of the uraniferous rock in southern Greenland the selective flotation of steenstrupine and other uranium and thorium-bearing minerals such as monazite from the Kvanefjeld Lujavrite was studied (Sørensen and Lundgaard, 1966). Experiments indicated that linoleic acid was a more efficient collector than oleic acid for these minerals.

Since 2008, metallurgical testwork has conducted by the company GME focusing on the recovery of both uranium and REEs and showed that REE and uranium bearing phosphate minerals can be concentrated into ten percent (10%) of the original mass with high recoveries. This enriched, so called, "REP" (Rare Earth Phosphate) concentrate has been shown to contain greater than 10% REO and 2000 ppm U3O8. The locked cycle and pilot

plant testwork has confirmed the results of the batch tests (Greenland Minerals and Energy Ltd., 2012). As one of the research targets in the EURARE project which is for development of a sustainable exploitation scheme for Europe's REE ore deposits new studies in mineralogy and beneficiation were conducted on the Kvanefjeld ore in GTK Mintec during the year 2012 to 2015.

Aero 6494, a hydroxamate collector developed by CYTEC, is more selective for REE-phosphate flotation than other collectors tested. The effects of grinding size, collector dosage, conditioning intensity (agitation speed), conditioning temperature and time, retention time at rougher stage on flotation performance of REE (La, Ce, Y) (recovery and selectivity) were investigated by laboratory bench testing. A REE concentrate with the grades of La 2.8%wt, Ce 5.1%wt and Y 1.0%wt and recoveries of 80.5% La, 79.8% Ce and 55.3% Y was obtained at the optimized conditions. Mineralogical analsis of the concentrate showed that steenstrupine was significantly enriched in the final concentrate. The beneficiation technique deveploed in laboratory was demonstrated in pilot sacle at GTK Pilot Plant in Outokumpu Finland. The technique included high intensity and temperature slurry conditioning after grinding the ore to 80% passing to 75 µm, rougher and scanvenger REP flotation using conventional agitation flotation machines and cleaner flotation using Jameson Cell Rigs.

The dominant rare earth bearing mineral present in Norra Kärr ore is Eudialyte. It is a complex sodium-zirconium-silicate which contains modest levels of rare earths. The main gangue minerals in the ore include four alkali-silicates: albite, aegirine, K-feldspar, and analcime. Mineralogical analysis showed the particle sizes of the minerals are quite fine at approximately 50 µm. But there are differences on magnetic susceptibility between the minerals which lends them to be separated by magnetic separation. Eudialyte is a weakly magnetic mineral better known as a paramagnetic mineral. Other paramagnetic mineral in the ore includes aegirine. Diamagnetic (non-magnetic) minerals are identified are mainly albite, K_feldspar and nepheline and catapleiite.

Beneficiation of eudialyte from the Norra Kärr ore was investigated (Yang and Krebs, 2016) by magnetic separation and flotation. The beneficiation flowsheets developed include : 1) Single high intensity magnetic separation flowsheet to directly recover eudialyte using Sala HGMS and Slon magnetic separator, and  2) Flotation-magnetic separation flowsheet, pre-floatation of silicates prior to recovery of eudialyte by magnetic separation.

The parameters tested include: grinding and regrinding size (P80= 60µm, 70µm, 90µm and 145 µm), desliming, flotation reagents including tallow amine (collector), Na-oleate (collector), Aero 6494 (collector) and Aero 3030C (promoter), magnetic intensity, HGMS intensity range: 0.05T-1.96T; Slon intensity: 0.3 T, 1.0 T and 1.2 T, magnetic matrix type for HGMS and Slon separator, HGMS matrix type XMO with aperture hole size 0.3 mm and XRO with aperture hole size 0.85 mm; Slon matrix with aperture hole size: 1.0 mm.), and pulsation for Slon Magnetic Separator, examined across a range of parameters, pulsation rates: 25 rpm, 50 rpm, 100 rpm and 150 rpm. Being the most economic and environmentally friendly one the beneficiation technique of high intensity magnetic separation using Slon Magnetic Separators was demonstrated in pilot scale in 2015 at GTK Pilot Plant in Outokumpu Finland.

As a large REE deposit located in Greenland the Kringlerne deposit has a similar mineralogy to that of Norra Kärr deposit with eudialyte as the REE host mineral and the similar suite of gangue minerals. But the eudialyte in the Kringlerne ore has much coarse grain size than that of the eudialyte in the Norra Kärr ore. Historical beneficiation testwork has shown that eudialyte is able to be concentrated by dry magnetic separation after crushing. This process included at least two stages of magnetic separation. Firstly, a roughing processing stage is employed which removes the non-magnetic minerals by operating the magnetic field at a high intensity.

Secondly, a cleaning stage is performed to separate eudialye from most other paramagnetic minerals. The beneficiation investigations in the project EURARE focused on the determination of magnetic field intensities in two stages and particle size effects. The technique was demonstrated in pilot scale. The sample was crushed by HPGR to 100% passing 600 μm and screened to produce size fractions of -600+260 μm, -260+53 μm and -53 μm. The fractions -600+260 μm and -260+53 μm were reported to dry magnetic separation by using an Eriez 24" Salient Pole Rare Earth Drum magnetic separator, an Eriez 12 inch diameter Rare Earth Roll Magnetic Separator. The final Eudialyte product was obatained containing 56.2% of the total zirconium (recovery), $ZrO_2$ grade 8.64% and mass yeild 25.29% (Eudialyte is a complex zirconium silicate. $ZrO_2$ assays were used as an indicator of REE content).

To maximize zirconium recovery, treatment of the -53 μm slimes product would be required, as this product contained 36.7% of the total zirconium content in the ore. Recovery of the weakly magnetic zirconium bearing mineral catapleiite is also a challenge for magnetic separation as it behaves like a feldspar.

## 22.3.2 METALLURGICAL EXTRACTION

### 22.3.2.1    CHEMICAL TREATMENT

In the leaching process used for Baotou rare earth concentrates in China the roasting starts with concentrated sulfuric acid at >300 °C. The rare earth sulfates formed during this process are then leached with water, and excess acid is neutralized with magnesia and filtered. The leach solution then proceeds to solvent extraction, alternatively a mixed rare earth chloride (for electrolysis to misch metal) could be produced by precipitation with ammonium carbonate, followed by dissolution with HCl and crystallization. The problems are: HF and sulfur dioxide report to the off-gas from roasting. Large amounts of water or alkaline solutions are needed to remove them, resulting in large volumes of acidic effluents; and the radioactive element, thorium, is precipitated and reports to the leach residue. It cannot be recovered economically, resulting in both loss of the valuable thorium and potential environment hazards.

The roasting process has been modified (Feng Xie et al., 2014), for example by adding MgO or CaO and NaCl to stabilize fluorine in the leaching residue instead of releasing it to the waste gas phase. Bastnesite has also been roasted with ammonium chloride, which decomposes into gaseous HCl that forms rare earth chlorides, which are readily leached with hot water. Another variant involves heating concentrate with sulfuric acid at 40–180 °C for two to four hours before roasting at 150–330 °C. This suppresses decomposition of sulfuric acid, resulting in a relatively high fraction of HF in the gas phase; this can be recovered as solid NH4F by reacting with (NH4)2CO3 in the off-gas pipe. In some plants, the bastnesite concentrates are first digested with concentrated NaOH to decompose carbonates and then leached with hydrochloric acid to produce mixed rare earth chlorides (Gupta and Krishnamurthy, 2005; Xu et al., 2012). The disadvantages of this process include high alkaline consumption and the radioactive thorium reporting to both the leachate and the residue, which hampers subsequent recovery.

### 22.3.2.2    REE SEPARATION

Solvent extraction

The separation of trivalent lanthanides as a group from actinides as well as individual lanthanides from each other is a formidable challenge in the field of separation science. The lanthanides are usually separated using

multistage extractions in counter-current mode in mixer settlers which are tedious and time consuming. Therefore, the development of new extraction systems for separation of lanthanides as a group or from one another using ion-specific compounds/solvents has also been reported. Several stages of mixer-settlers are employed for their separation on industrial scale. For leached solutions containing low concentration of rare earth metals, different ion exchange cationic or anionic resins are employed depending on the constituent of the aqueous solution using batch or continuous mode in column. The purified solution obtained after separation could be further processed to produce the value added products in the form of salt for industrial application.

Worldwide, extensive studies have been carried out for the extraction of various rare earth metals by solvent extraction process using different organic extractants in order to develop efficient process for their separation from different feed solutions.

Rare earth extraction by SX including modeling of the process using different extractants has been reviewed (Thakur, 2000). These studies have been classified based on the solution generated by the treatment of rare earths containing materials as chloride, nitrate, thiocyanate, phosphate, etc. The properties of their extraction and separation, formation of complex, separation factor, etc. have been highlighted in the present review paper by different research and academic institutions (Manis Kumar Jha et al., 2016).

Ion exchange and Precipitation

Zeolites are well-known for their ion exchange capabilities that would be potentially applicable for the REEs separation. The study (Lucie Duplouy, 2016) primarily investigated the ion exchange behavior of REEs onto several types of zeolites, namely the Ferrierite, the Faujasite and the Linde Type L. These zeolites were chosen because of their altered framework type and controllable charge density through synthesis. The commercially available zeolites were systematically characterized by means of X-Ray Diffraction (XRD), Energy Dispersive X-ray spectroscopy (EDX) and Attenuated Total Reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR). Lanthanum was chosen as the model REE. The pH-uptake behavior of La on zeolites was studied extensively. Results showed that among all our selected zeolites, only LTL gave reasonable amount of La ion exchange capacity (0.16 mmol/g at pH 3). Subsequently, the ion exchange isotherm of La on LTL was described at pH 3. The isotherm followed Langmuir type with a maximum capacity of 0.25 mmol/g. An equimolar ternary mixture of lanthanum, neodymium and dysprosium was used to test the selectivity of LTL zeolite towards different REEs. Results suggested that the uptake sequence followed La > Nd > Dy, which indicated the decrease of capacity with increased atomic number. Almost all the REEs could be leached off from the REE loaded zeolites with a pH 1.51 nitric acid solution.

Adsorption

Among the available methods, adsorption has gained wider attention because of its simplicity, high efficiency and low cost. Ioannis Anastopoulos et al. (2016) reviewed the recently published literature (after 2013) regarding the removal of rare earth metals fromaqueous solution by different low cost adsorbents. Adsorption was found to be influenced by contact time, adsorbent dose, initial concentration, solution pH and temperature.

## 22.4 CHARACTERIZATION OF MINING TAILINGS AND PROCESSING RESIDUES AND POTENTIAL UTILIZATIONS

## 22.4.1 MINE REE CONTAINING TAILINGS

The underderflow of tailings thickener in LKAB Kiruna concentrator was assayed and the main elements' and REE analyses are shown in Table 8 (T. Karlkvist, 2017).

Table 8 Te compositions of main elements and REE in the tailings of LKAB Kiruna concentrator

| Main element | % | REE | mg/kg |
|---|---|---|---|
| SiO2 | 45.80 | Sc | 35.6 |
| Al2O3 | 8.37 | Y | 178 |
| CaO | 14.61 | La | 339 |
| Fe2O3 | 10.41 | Ce | 627 |
| K2O | 1.95 | Pr | 70.9 |
| MgO | 6.86 | Nd | 256 |
| MnO | 0.22 | Sm | 40.9 |
| Na2O | 2.82 | Eu | 5.84 |
| P2O5 | 6.38 | Gd | 36.9 |
| TiO2 | 1.25 | Tb | 5.03 |
| L.O.I | ~4 | Dy | 26.9 |
| | | Ho | 5.85 |
| | | Er | 16.1 |
| | | Tm | 2.14 |
| | | Yb | 13.4 |
| | | Lu | 2.10 |
| | | Total | 1661 |

LKAB was investing the tailins ponds at the Kiruna and the Malmberget operations, these ponds were thought to contain large quantities of REE bound in the phosphate mineral apatite, which is considered an impurity in iron ore. Tailings ponds at both Kiruna and Mamberget are rich in apatite, a phosphorous mineral, and with rare earth. LKAB planned to conduct a study to determine the conditions for the recovery of apatite and REE from the tailings in the ponds. Test drilling results indicated the occurrence of 15 REE in the apatite. Estimates showed that there was enough apatite in the tailings ponds for the production of 400,000 t/yr of apatite concentrates for a period of 14 years (Alberto Alexander Perez, 2013).

Potential REE Potential deposits at LKAB (Susanne Rostmark and Andreas Fredriksson, 2016) are shown in Table 9.

Table 9 Potential REE Potential deposits at LKAB

| Deposit | % P | REO% | REE% |
|---|---|---|---|
| Kiruna | 13.1 | 0.99 | 0.83 |
| Malmberget | 16.3 | 0.95 | 0.79 |
| Leveäniemi | 10.8 | 0.51 | 0.43 |
| Lappmalmen | 12.1 | 0.93 | 0.77 |
| Nukutusvaara | 15.1 | 0.98 | 0.81 |

| Haukivaara | 11.2 | 0.75 | 0.92 |
| Mertainen | 13.2 | 0.4 | 0.33 |
| Pattok | 8.5 | 0.4 | 0.34 |

REE from Kiirunavaara exist in apatite, monazite, allanite and titanite. Apatite, the main mineral for phosphorus, and REE, can be enriched via flotation; monazite, contains REE and is enriched together with apatite, but also by WHIMS (wet high intensity magnetic separation); allanite and titanite, silicate minerals. LKAB has found a way to separate calcite and apatite. At the best flotation conditions the apatite concentrate grade >30% P2O5 at a high recovery 70%. But the REE recovery was about half of that of apatite. Further work necessary includes investigating other deposits which may be interesting from an apatite/REE point-of-review, and materials handling, grinding influence, de-sliming, temperature, process water chemistry, flotation of other REE containing minerals, etc.

## 22.4.2 PHOSPHOGYPSUM

Phosphogypsum is the main by-product of the production of phosphoric acid ($H_3PO_4$) by sulphuric acid ($H_2SO_4$) digestion of a concentrated slurry of pulverised phosphate ores. Apatite is the main phosphate mineral in most phosphate deposits (Rutherford et al., 1994). In sedimentary phosphate rock, apatite occurs in an amorphous form: francolite. Francolite has a complex chemical composition and can be represented by the formula $(Ca,Mg,Sr,Na)_{10}(PO_4,SO_4,CO_3)_6F_{2-3}$.. In igneous phosphate rock, apatite occurs as the variety fluorapatite, $Ca_{10}(PO_4)_6F_2$. Phosphate rock also contains trace amounts of many other elements, including thorium, uranium and rare earths. The rare-earth content depends on the type of phosphate rock. Sedimentary phosphate rock contains 0.01-0.1 wt% of rare earths, but also about 0.01 wt% of uranium. Igneous phosphate rock is much richer in rare earths than sedimentary phosphate rock (1-2 wt%) and contains only very small amounts of uranium (Koen Binnemans et al., 2015). Analysis of phosphate rock from Florida gave a total rare-earth content of 0.059%, with the main elements being lanthanum (0.015 wt%), cerium (0.012 wt%), yttrium (0.011 wt%) and neodymium (0.007 wt%). The scandium concentration was very low: 0.0003 wt% (3 ppm). It was estimated that the 6 million tonnes of phosphate rock that have been processed in the USA in 1964 could have yielded 3500 tonnes of rare earths (cf. estimated worldwide REO production in 2013: 110,000 tonne (Gambogi, 2014). The rare-earth content depends on the type of phosphate rock (Habashi, F., 1985, 1998). The total REE oxide concentrations in different phosphate ores are shown in Table 10.

Table 10 The total REE oxide concentrations in different phosphate ores

| Locality | Total rare-earth oxides (wt%) |
| --- | --- |
| Kola (Russia) | 0.8-1.0 |
| Florida (USA) | 0.06-0.029 |
| Algeria | 0.13-0.18 |
| Morocco | 0.14-0.16 |
| Tunesia | 0.14 |
| Egypt | 0.028 |
| Vietnam | 0.031 |

Depending on the production method, the phosphogypsum formed primarily consists of either calcium sulphate dihydrate, $CaSO_4 \cdot 2H_2O$ (gypsum) or calcium sulphate hemihydrate, $CaSO_4 \cdot 1/2H_2O$, and it contains also small amounts of silica, fluoride compounds and unreacted phosphate rock. The amount of phosphogypsum produced during phosphoric acid production exceeds the mass of the product, i.e. 4.5-5.5 tonnes of phosphogypsum are generated per tonne of phosphorus pentoxide ($P_2O_5$) (El-Didamony et al., 2012).

The rare earths are concentrated in phosphogypsum during the production of phosphoric acid. About 70-85% of the rare earths originally present in the phosphate rock end up in the phosphogypsum. The remainder stays dissolved in the leaching solution, which also contains the phosphoric acid. A smaller part of the rare earths is incorporated in the phosphogypsum if the leaching is performed at lower temperatures or with less concentrated $H_2SO_4$ (Habashi, 1985). The average concentration of rare earths in phosphogypsum is 0.4 wt% (Habashi, 1985). However, the estimated global production of phosphate rock in 2013 was 224 million tonnes (Jasinski, 2014), so that the total amount of rare earths in the mined phosphate rock is also large in absolute terms. This indicates that phosphate rock and the derived product phosphogypsum may become valuable sources of rare earths in the near future, provided the rare-earth prices are high enough. In comparison with red mud, phosphogypsum contains lower concentrations of scandium. The concentrations of REE in different phosphogypsums are presented in Table 11.

Table 11 Concentrations of REE in phosphogypsum samples

| REE | Concentration[1], ppm | Concentration[2], ppm | Concentration[3], ppm |
|---|---|---|---|
| La | 1450 | 289.7 | 476-500 |
| Ce | 2310 | 878.6 | 1231-1289 |
| Pr | 235 | 114.5 | 141-149 |
| Nd | 899 | 469.2 | 711-738 |
| Sm | 163 | 70.6 | 138-143 |
| Eu | 34.9 | 16.9 | 24-28 |
| Gd | 98.7 | 45.0 | 86-93 |
| Tb | 7.45 | 4.3 | 8.3-9.3 |
| Dy | 45.5 | 15.2 | 29-32 |
| Ho | 7.37 | 2.1 | 2.9-3.1 |
| Er | 15.7 | 4.3 | 6.83-7.7 |
| Tm | 1.36 | 0.3 | 0.8-1.03 |
| Yb | 5.6 | 1.1 | 1.0-1.25 |
| Lu | 0.568 | 0.1 | <0.43 |
| Y | 180 | 36.0 | 1.43-7.9 |
| Sc | 1.21 | <0.5 | 71-83 |
| Total | 5455 | 1948.0 | 2935-3085 |

[1]the Belgian company Prayon SA, dried at 250 °C (Germeau et al., 2013); [2]PG sample from Siilinjärvi mine, Finland, and [3]South Africa PG from Richards Bay plant (Yang, 2017)

## 22.4.3 BAUXITE RESIDUE (RED MUD)

Bauxite, a mixture of impure hydrated aluminium oxides, is the most important aluminium ore. The estimated global production of bauxite in 2013 was 259 million tonnes (Bray, 2014). Aluminium metal is produced from pure Al2O3, which is obtained via the Bayer process, where bauxite is digested in a concentrated NaOH solution at temperatures and pressures. In the world there is an annual bauxite residue production of $1.2 \times 10^8$ tonnes (dry matter) and a total inventory of $3 \times 10^9$ tonnes (International Aluminium Institute, 2013).

All rare earths end up in the bauxite residue during the processing of bauxite by the Bayer process, because these elements are associated with iron and titanium minerals that remain unchanged (Binnemans, K. et al., 2015). The average concentrations of rare earths in Greek bauxites and bauxite residues are shown in Table.

The average concentrations of rare earths (including scandium) in Greek bauxites and bauxite residues are shown in Table 12 (Ochsenkühn- Petropoulou et al., 1994).

Table 12 The average concentrations of REE (including scandium) in Greek bauxites and bauxite residues

| Element | Bauxite | Bauxite residue |
|---------|---------|-----------------|
| La | 87.2 | 149.0 |
| Ce | 224.3 | 418.0 |
| Pr | 13.9 | 25.8 |
| Nd | 62.4 | 115.0 |
| Sm | 13.2 | 28.9 |
| Eu | 2.5 | 5.0 |
| Gd | 12.8 | 23.3 |
| Tb | n.d. | n.d |
| Dy | 7.0 | 12.8 |
| Ho | 2.0 | 4.3 |
| Er | 8.1 | 17.2 |
| Tm | n.d. | n.d. |
| Yb | 8.0 | 15.6 |
| Lu | 1.4 | 2.4 |
| Y | 55.9 | 93.9 |
| Sc | 59.0 | 127.9 |

The estimated totals of REE in Greek bauxites and bauxite residues are 506 ppm and 1040 ppm, respectively (Ochsenkühn- Petropoulou et al., 1994). The rare-earth concentration in Jamaican red mud varies between 1500 and 2500 ppm (Wagh and Pinnock, 1987).

Very little information is available on the mineralogy of the rare earth- rich phases in red mud. Allanite-(La) and dissakisite-(Ce) were identified as the rare-earth phases in an Indian bauxite residue sample, containing 70 ppm of lanthanum and 100 ppm of cerium (Abhilash et al., 2014).

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## 23  SCANDIUM (SC)

### 23.1 PRODUCTION LINES OF IDENTIFICATION FROM PRIMARY RESOURCES

#### 23.1.1 SC, PRODUCTION AND APPLICATIONS

Scandium is a chemical element with symbol Sc and atomic number 21. Scandium is a soft metal with a silvery appearance and has historically been sometimes classified as a rare-earth element, together with yttrium and the lanthanides. It was discovered in 1879 by spectral analysis of the minerals euxenite and gadolinite from Scandinavia.

Applications for scandium were not developed until the 1970s. The positive effects of scandium on aluminium alloys were discovered in the 1970s, and its use in such alloys remains its only major application. The world production of scandium is in the order of 10 tonnes per year, in the form of scandium oxide. The demand is about 50% higher, and both the production and demand keep increasing. In 2003, only three mines produced scandium: the uranium and iron mines in Zhovti Vody in Ukraine, the rare-earth mines in Bayan Obo, China, and the apatite mines in the Kola peninsula, Russia; since then many other countries have built scandium-producing facilities. In each case scandium is a byproduct from the extraction of other elements and is sold as scandium oxide (https://en.wikipedia.org/wiki/Scandium).

Various independent authors quote global market scandia volumes of 2-10 tonnes per year. EMC believes the current (2014) market supply is at least 15 tonnes per year. This estimate is based on 6 discussions with potential customers, the level of metals trader activity and interest, and the fact that certain scandium consumers are believed to be sourcing their own scandium through small controlled recovery operations. This estimate doesn't consider scandium contained in master alloy currently being sold from Russian stockpiles (Duyvesteyn and Putnam, 2014).

Principal uses for scandium are in solid oxide fuel cells (SOFC's), high-strength aluminum alloys, highintensity metal halide lamps, electronics, and laser research (Duyvesteyn and Putnam, 2014).

Solid Oxide Fuel Cells (SOFC's) – Scandia can substitute for yttria as a stabilizing agent for the solid electrolyte (typically zirconia) in the fuel cell. The substitution allows reactions to occur at lower temperatures, extending the life of the components and increasing the power density of the unit.

Metallurgy - Scandium readily alloys with aluminum and modifies the grain structure of the combined metal, dramatically increasing strength without sacrificing corrosion resistance, while offering enhanced weldability--- something typically lost in the alloying process of high performance aluminum alloys.

Ceramics - The addition of about 20% scandium carbide to titanium carbide results in a doubling of the hardness of the mixed Ti-Sc carbide, to about 50 GPa, second only to diamonds in hardness.

Electronics - Scandium is used in the preparation of the laser material $Gd_3Sc_2Ga_3O_{12}$, gadolinium scandium gallium garnet (GSGG). This garnet when doped with both Cr and Nd ions is said to be 3 1/2 times as efficient as the widely used Nd doped yttrium aluminum garnet laser. Ferrites and garnets containing scandium are used primarily in switches in computers. These magnetically controlled switches work by undulating light passing through the garnet and microwave equipment.

Lighting – Scandium is used in mercury vapor high-intensity lights to create natural light. Scandium has a broad emission spectrum that generates a 'daylight' effect desirable for camera lighting, movie and television studio lights.

Phosphorus/Displays - Scandium compounds have application as a host for phosphorus or as the activator ion in TV or computer monitors. Sc2O3 and ScVO4 are typical host materials, while ZnCdS2, activated with a mixture of silver and scandium, creates a red, luminescent phosphorus suitable for use in television displays. The current cost of scandium typically dictates the use of other materials in these applications.

## 23.1.2 PRIMARY RESOURCES FOR SC PRODUCTION

In Earth's crust, scandium is not rare. Estimates vary from 18 to 25 ppm, which is comparable to the abundance of cobalt (20–30 ppm). However, scandium is distributed sparsely and occurs in trace amounts in many minerals. Madagascar and Iveland-Evje region in Norway have the only deposits of minerals with high scandium content, thortveitite $(Sc,Y)_2(Si_2O7)$ and kolbeckite $ScPO_4 \cdot 2H_2O$, but these are not being exploited (USGS, 2015). Scandium is present in most of the deposits of rare-earth and uranium compounds, but it is extracted from these ores in only a few mines worldwide. The other minerals containing Sc include bazzite $(Be(Sc, Al)2Si6O18)$, cascandite $(Ca(Sc, Fe2+)Si3O8(OH))$, Jervisite $NaSc3+[Si2O6][1]$ $(Na,Ca,Fe2+)(Sc,Mg,Fe2+)Si2O6)$, Juonniite $(CaMgSc(PO4)2(OH)\bullet4(H2O)$, magbasite $(KBa(Al, Sc)(Mg, Fe2+)6Si6O20F2)$, Pretulite $(ScPO4)$, Scandiobabingtonite $(Ca2(Fe2+, Mn)ScSi5O14(OH))$, titanowodginite $(Mn2+(Ti,Ta,Sc)2O8)$, and heftetjernite $(ScTaO4)$ (Duyvesteyn and Putnam, 2014).

Most of today's scandium production tends to come as a byproduct of the leaching activity associated with production of other metals, minerals, or rare earths, specifically U, Th, Al, W, Sn, Ta, P and REEs (Duyvesteyn and Putnam, 2014). Scandium is distributed in trace amounts in many ores such as wolframite [(Fe,Mn)WO4]' titaniferous magnetites, tinstone (SnO2), bauxite and uranium ore and is generally obtained as a byproduct from the processing of these ores (Guo G., 1988).

The main valuable scandium resources are effluents or slags which form during processing of uranium, iron, tungsten, nickel, tin, titanium, zirconium, tantalum, aluminum and other rare earth elements. The annual production of scandium is around 5-12 tons and the price of 99.9% Sc2O3 ranges between 2000-3000$ per kg. The production rate cannot reach to high levels due to the main supply of scandium as a by-product of other metals (Ece Ferizoğlu et al., 2016).

The principal Sc-producing countries today are China, Russia, Ukraine, and Kazakhstan (Duyvesteyn and Putnam, 2014).

Resources are known in Australia, China, Kazakhstan, Madagascar, Norway, Russia, and Ukraine. Resources in Australia are contained in nickel and cobalt resources in New South Wales. China's resources are in tin, tungsten, and iron deposits in Jiangxi, Guangxi, Guangdong, Fujian, and Zhejian Provinces, and is currently produced from the Bayan Obo deposit of REE. Resources in Russia and Kazakhstan are found in certain uranium-bearing deposits, and on the Kola Peninsula in apatites. In the Ukraine, scandium was previously recovered as a byproduct of iron ore processing at Zheltye Voda. Scandium in Madagascar and Norway is typically found in pegmatite formations containing thortveitite (Duyvesteyn and Putnam, 2014).

The Bayan Obo Nb/REE/Fe mine complex in Inner Mongolia, China represents a significant source of scandium production today, although it is not known what the scandia production rate is from this deposit. The deposit is

large (18 km x 4 km), and extremely complex, with deposition, mineralization, metamorphism and intrusions occurring over a suspected four different metallogenitic periods. The deposit exhibits over 190 known mineral species, and can also produce both scandium and thorium. The various ore types at the deposit have different scandium contents, ranging from 40 ppm to 169 ppm. Higher scandium contents are observed in REE tailings, where grades can reach 250 ppm (Duyvesteyn and Putnam, 2014).

The absence of reliable, secure, stable, and long-term production has limited commercial applications of scandium. Because of its rarity, it is among the most expensive elements. Price for pure scandium fluctuates between 4 000 and 20 000 US dollars per kilogram   (https://en.wikipedia.org/wiki/Scandium).

## 23.2 PROCESSING TECHNIQUES RECOGNITION AND ANALYSIS

### 23.2.1 MINERAL PROCESSING

Most of today's scandium production tends to come as a byproduct of the leaching activity associated with production of other metals such as U, Th, Al, W, Sn, Ta, P and REEs (Duyvesteyn and Putnam, 2014). Scandium is distributed in trace amounts in many ores such as wolframite, titaniferous magnetites, tinstone ($SnO_2$), bauxite, uranium and REE ores. Sc is generally obtained as a byproduct from the processing of these ores (Guo G., 1988).

### 23.2.2 METALLURGICAL PROCESSING

Pyrometallurgy is a suitable technology for recovery of scandium from its ore containing high scandium content. However, the  high  energy consumption and environmental  pollution  are  considered  to  make  this technology  to  be  less  attractive. Hydrometallurgical technology is an alternative method  to the traditional pyrometallurgy for recovery of metals from primary and secondary sources because  of its advantages such as low capital cost with suitability for small  scale application, reduced environmental degradation and high  metal recoveries. In hydrometallurgy, leaching is a fundamental  process using lixiviants such as  acids (sulfuric, hydrochloric, nitric acid), cyanide, thiosulfate or alkaline  solutions, to dissolve desired  metals. There  are several  techniques  to  separate  and  recover  the  rare  earth  metals  from  aqueous  media  such  as precipitation,  solvent  extraction,  adsorption  and  ion  exchange resin, etc. (Nghiem Van Nguyen et al., 2015).

Recovery of scandium from chloride media using the novel ion exchange resin was studied (Nghiem Van Nguyen et al., 2015). In order to carry out the adsorption  studies, the synthetic solutions containing  scandium, cerium, lanthanum and aluminum  of 20, 750, 300 and 2000  mg/L  were prepared similarly  to the composition of the  chloride solution  generating  in the  rare earth  extraction processing  of monazite, by dissolving metals chloride  in  de-ionized  water. The  resin  (provided by a Japanese company) was  found  to  adsorb  effectively and  selectively  scandium(III)  at  pH  1,  and  the  adsorption  selectivity  of the resin for scandium among the mixture  is suggested from the pore size of the resin beads. The kinetic adsorption of scandium by the resin is slow, and contact time 24 hours was chosen as a suitable time in this study.  Scandium loaded on the resin can be eluted completely by 2 M HCl eluent at temperature 80°C.

Wolframite residue, which is produced during a process using the alkali digestion of wolframite to extract tungsten, often contains approximately 0.02% scandium oxide and is one of the major scandium-bearing resources. To recover scandium from the wolframite residue, several processing routes have been proposed. For example, for wolframite residue decomposed with sulfuric acid, scandium was separated from iron, manganese and titanium by processing the resulting leach liquor with carbonate and was extracted with diethyl

ether from sulfocyanate solution.' Alternatively, scandium has been extracted with primary amine- or with alkylphosphoric acids" directly from the leach liquor.

Hydrochloric acid was also used to decompose the wolframite residue, and di-(2-ethylhexyl) phosphoric acid in kerosene was used to extract scandium from the resultant leach liquor (Guo G. et al., 1988). The recovery of scandium (as a hydroxide) from wolframite residue mainly involves leaching, followed by extraction, scrubbing and stripping (Figure 1). The wolframite residue, before being leached with hydrochloric acid, was ground to -300 mesh and washed with water to approximate neutrality and reduce acid consumption during leaching.

Since scandium is probably present in the form of hydroxide in the residue, it can be converted to soluble scandium salts by leaching the residue with various mineral acids such as hydrochloric acid, sulfuric acid and nitric acid. Hydrochloric acid was chosen to leach the residue because it is relatively inexpensive and can leach scandium preferentially to other metals as a result of the formation of strong scandium complexes with the chlorine ion. Hydrochloric acid is also a good medium for extracting scandium with D2EHPA in kerosene, and the slurry resulting from the leaching of the residue with HCl can be easily filtrated since only a small amount of silica is generated.

Leaching tests were performed at 100°C for two hours by adding different amounts of hydrochloric acid and water to vary the ratios of residue to acid and liquid to solid. As the leaching operation neared completion, a small amount of alum or polyglycol was added to the slurry to promote the coagulation of silica. Leaching temperature or time influenced scandium extraction only minimally. However, acid addition and the ratio of liquid to solid during leaching had a significant impact (Tables III and IV). At a specified ratio of liquid to solid, as acid addition increased, there was a fairly large increase in scandium extraction. When the ratio of residue to acid addition was raised from 1:1 to 1:2, scandium extraction increased from 66.9% to 95.3%. However, the ratio of liquid to solid during leaching had a greater effect on scandium extraction than the ratio of residue to acid addition.
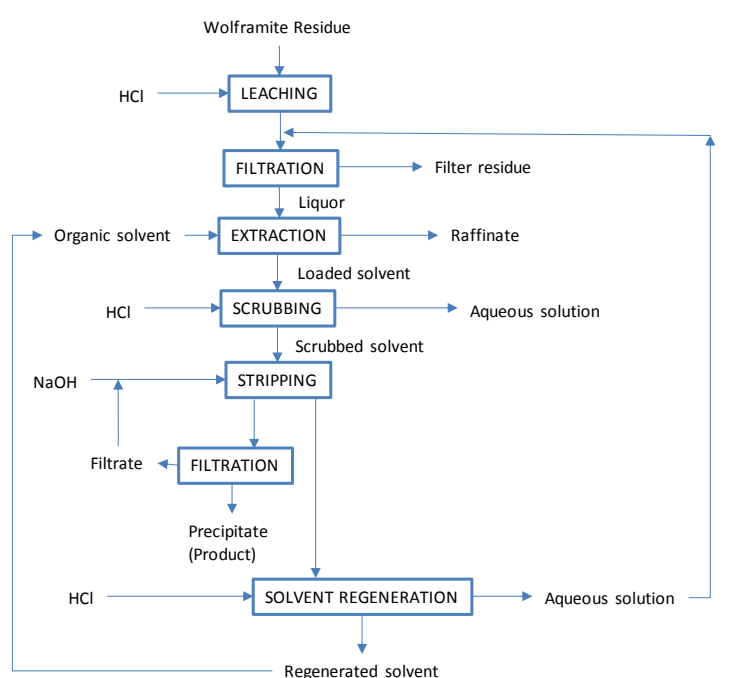


Figure 1. Flowsheet for the recovery of scandium from wolframite residue (Guo G., et al., 1988)

The organic solvent consisted of di-(2-ethylhexyl) phosphoric acid (D2EHPA), sec-octylalcohol and odorless kerosene, which were used as an extractant, a modifier and a diluent, respectively.

Scandium can be also recovered as a by-product from the hydrometallurgical extraction process of lateritic nickel cobalt ores. The high pressure sulphuric acid leaching (HPAL) behavior of typical lateritic ore was studied previously (Kaya S. and Topkaya Y.A., 2014). The studied lateritic ore contained 106 g/t scandium and 80.6% scandium in the ore could be extracted into leach solution together with nickel, cobalt and other impurities. A study (Ece Ferizoğlu eta l., 2016) was conducted to obtain maximum scandium precipitation and recovery with minimum nickel and cobalt co-precipitation. In accordance with the aim of the study, the optimum pH was determined for each precipitation step and then the scandium enriched precipitate was tried to be re-leached under the determined optimum conditions. According to the experimental findings, if 1st impurity removal step is conducted at 90°C, pH 2.75 for 120 minutes and 2nd impurity removal is done at 60°C, pH 4.75 for 180 minutes, scandium can be precipitated and separated efficiently from MHP circuit with minimum nickel-cobalt losses after two-step pH controlled precipitation process. After the precipitation and concentration, scandium can be re-leached efficiently, if the re-leach process is conducted at 60°C for 60 minutes with 100 g/L of $H_2SO_4$ acid with 0.2 solid to acid-water mixture ratio. In the future, scandium is being planned be recovered from the purified re-leach solution by ion exchange and/or solvent extraction methods.

A study (Nghiem Van Nguyen et al., 2015) focused on separation and recovery of scandium from chloride solution using the new synthesized ion exchange resin. The resin containing glycol amic acid groups shows the possibility to recover scandium from chloride aqueous solutions. At pH 1, the adsorption selectivity of scandium can be obtained among the others metals. The kinetic adsorption of scandium by the resin was found slowly, and contact time 24 hours was chosen as a suitable time in this study. The elution of scandium from the loaded resin could be completed with 2 M HCl solution at 80°C. The close process will be established based on the optimum parameters which are obtained throughout this investigation, and that process can be applied in metal extraction processing for recovery of scandium and the other rare earth metals using the novel ion exchange resin.

Bengi Yagmurlu et al. (2016) researched an alternative method for scandium (Sc) recovery from impure bauxite residue solutions containing Fe(III), Al, Ca, Nd, and Y through the use of hydroxide and phosphate precipitation. Among hydroxide donors, ammonia solution removed the most Fe(III) from solution, while co-precipitation of other elements in the synthetic pregnant leach solution remained negligible. When using dibasic phosphate as the precipitant, in the pH range of 1.5–2.5, both Sc and Fe were removed rapidly, while co-precipitation of other ions remained low. Experimental results were used to propose the preliminary design of a three-stage precipitation process capable of producing a scandium product from highly impure process solutions.

## 23.3 CHARACTERIZATION OF MINING TAILINGS AND PROCESSING RESIDUES AND POTENTIAL UTILIZATIONS

In the US, the fluorite tailings from the Crystal Mountain deposit near Darby, MT., are known to contain thortveitite and associated scandium-enriched minerals. Smaller scandium resources are contained in tungsten, molybdenum, and titanium minerals from the Climax molybdenum deposit in Colorado. Other lower grade domestic resources are present in ores of aluminum, cobalt, iron, molybdenum, nickel, phosphate, tantalum, tin, titanium, zinc, and zirconium. Process residues from certain historic tungsten operations in the United States also contain significant amounts of scandium (Duyvesteyn and Putnam, 2014).

One other potentially significant scandium resource is the red mud tailings from the Bayer process, employed in bauxite processing into alumina. Red mud tailings typically contain 50-110 ppm Sc, but certain locations show concentrations of 150 ppm, depending on the ore type and precise process route. The processes that

essentially double the original concentration of scandium (typically 30-50 ppm) also concentrate numerous other metals, specifically iron, aluminum and titanium, which are energy and process intensive to separate from scandium. Consequently, scandium recovery from these environmental legacy residues can be problematic, both as to environmental issues and cost (Duyvesteyn and Putnam, 2014).

Higher scandium contents are observed in REE tailings, where grades can reach 250 ppm at the Bayan Obo rare earth (Nb/REE/Fe) mine (Duyvesteyn and Putnam, 2014).

Wolframite residue, which is produced during a process using the alkali digestion of wolframite to extract tungsten, often contains approximately 0.02% scandium oxide and is one of the major scandium-bearing resources.

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## 24  SILICON METAL

### 24.1 PRODUCTION LINES OF IDENTIFICATION FROM PRIMARY RESOURCES

#### 24.1.1 GLOBAL PRODUCTION

Silicon is the second most abundant element in the Earth's crust. It is commonly found in rocks, sand, clays and soils, combined with either oxygen as silicon dioxide or with oxygen and other elements as silicates. [1], [2] So far, mainly quartz or quartzite is used for the extraction of silicon for ferrosilicon and silicon metal production. Though silica accounts for 66.62% of the mass of the upper crust, not all of it is readily for silicon metal production. This is due to the fact that silicon metal production requires high purity quartz or quartzite.[1] For silicon metal production the quartz or quartzite should contain at least 99.5% silica ($SiO_2$), while the impurities should be low ($Fe_2O_3$ 0.05-0.10%, $Al_2O_3$ 0.10-0.20%, $TiO_2$ <0.006%, CaO <0.2%, MgO < 0.2% and P being avoided).[3]

The global mine production of silicon metal is dominated by China (61%), followed by other countries, such as Brazil, Norway, United states, France, etc., as shown in **Figure 20**. The leading global silicon metal producers are listed in **Table 8**. According to U.S. Geological Survey, global resources for making silicon metal and alloys are adequate to supply world requirements for many decades.[4] The 5 year average European production of silicon metal between 2010 and 2014 was 195000 tonnes per year, which accounts for less than 10% of the global production. EU is a net importer of silicon metal.[1]
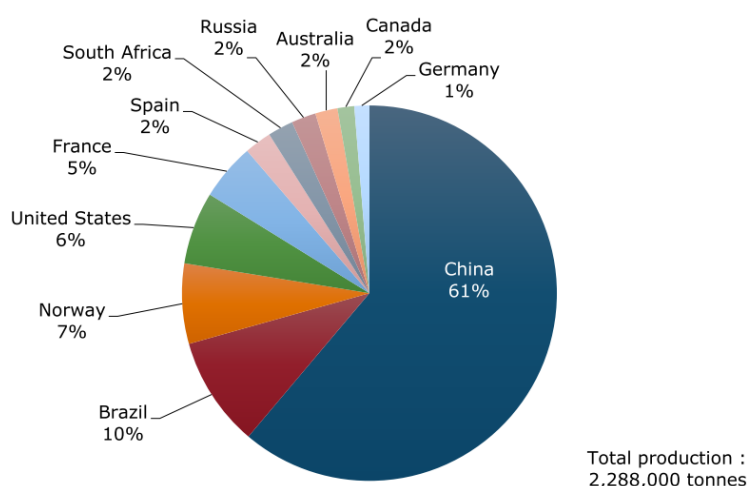


**Figure 20** Global mine production of silicon metal (average 2010-2014).[1]

**Table 8** Leading silicon metal producers in the world.[5]

| Country | Company | Production capacity | Production in 2013 | Production in 2014 |
|---------|---------|---------------------|--------------------|--------------------|
|         |         | in thousand tons    |                    |                    |
| China | Xinjiang Hoshine Silicon Industry Co. Ltd. | 260 | 147 | 200 |

| | Heihe Hoshine Silicon Industry Co. Ltd. | 96 | 40 | 52 |
|---|---|---|---|---|
| | Hubei Sanxin Silicon Co. Ltd. | 160 | 20 | 15 |
| | Gansu Sanxin Silicon Co. Ltd. | 80 | 40 | 36 |
| | Bluestar Silicon Material Co. Ltd. | 66 | 38 | 51 |
| Brazil | Rima | 80 | 68 | 45 |
| | CCM | 45 | 40 | 25 |
| | CBCC | 40 | 35 | 20 |
| | Liasa | 55 | 40 | 25 |
| USA & Canada | Global Metallurgical | 200 | 136 | 155 |
| Norway | Elkem | 150 | 105 | 115 |
| Spain, South Africa, France | Ferroatlantica | 260 | 200 | 220 |
| Russia | OOO Sual-Kremniy-Ural | 50 | 40 | 40 |
| | ZAO Kremniy | 50 | 25 | 30 |
| Australia | Simcoa | 33 | 25 | 25 |

## 24.1.2 APPLICATIONS OF SILICON METAL

Silicon metal is used to produce aluminum alloys, silicones & silanes, solar products, semiconductors and the other miscellaneous (such as explosives, refractories and advanced ceramics. The shares of different applications are shown in **Figure 21**. There are two types of aluminum alloys which contains silicon as the alloying elements. The first one is aluminum casting alloys with a silicon content typically ranging 7-12%. The second one is aluminum wrought alloys with a silicon content typically ranging 0.5-1.0%.[1], [6], [7] Silicones are synthetic compounds made up of repeating units of siloxane, which is a chain of alternating silicon atoms and oxygen atoms, frequently combined with carbon and/or hydrogen; in general it has the chemical formula $[R_2SiO]_n$, where R is an organic group such as an alkyl (methyl, ethyl) or phenyl group. Silanes is colorless, flammable gas. Both silicones and silanes are made from silicon metal.[8], [9] For solar and electronic applications the silicon (either polycrystalline silicon or monocrystalline silicon) ingots are sliced into thin silicon wafers and used for the production of solar cells, integrated circuits and other semiconductor devices.[10] The fields to which the silicon metal can be used depend on the grades of silicon metal, as shown in **Table 9**.

1.8 million tonnes in 2010
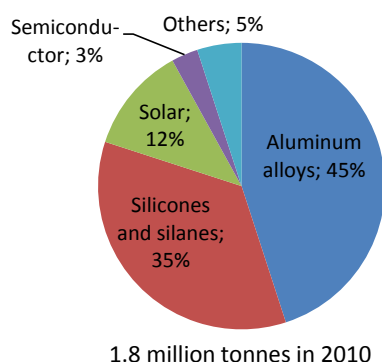
**Figure 21** Global end-uses of silicon metal produced in 2010.[11]

**Table 9** Typical chemical analyses of silicon metal products for various applications.[12]

| Element | Metallurgical-grade silicon (ppm) | Solar-grade silicon (ppm) | Polycrystalline solar-grade silicon | Electronic-grade silicon (ppm) |
|---|---|---|---|---|
| Si* | 99 | 99.999 9 | 99.999 99 | 99.999 999 999 |
| Fe | 2 000–3 000 | <0.3 | | <0.01 |
| Al | 1500–4 000 | <0.1 | | <0.0008 |
| Ca | 500–600 | <0.1 | | <0.003 |
| B | 40–80 | <0.3 | | <0.0002 |
| P | 20–50 | <0.1 | | <0.0008 |
| C | 600 | <3 | | <0.5 |
| O | 3000 | <10 | | |
| Ti | 160–200 | <0.01 | | <0.003 |
| Cr | 50–200 | <0.1 | | |

## 24.2 PROCESSING TECHNIQUES RECOGNITION AND ANALYSIS

### MINERAL PROCESSING

As described earlier, quartzite and quartz are usually used for the production of silicon metal. Quartzite is obtained by blasting operations in a quarry/mine while quartz is obtained by non-blasting operations through surface excavation of unconsolidated material (gravel quartz). The mineral processing of quartzite or quartz includes several fragmenting steps. The first step of the fragmenting is coarse crushing (primary crushing) by using e.g. a jaw crusher. Normally the crushing of quartzite requires less energy, since micro cracks in the rocks quartz are introduced during the blasting operation. However, for crushing the gravel quartz more energy would be required as the gravel quartz has gone through natural selection and only the strongest quartz boulders "survive" the size reduction during transportation in the river. For the first-step crushing, characteristic grain size ($d_{80}$) for the feed is usually 300-1000 mm while the product $d_{80}$ is 50-300 mm. After the first-step crushing the materials are screened, washed and the coarse fraction is further crushed to meet the market requirements (20-150 mm for the production of silicon metal in the submerged arc furnace). The fine materials that generated through the mineral processing are usually regarded as residual materials, which can either be disposed or

further screened to create fractions that can be sold or even given away, e.g. to the local community as filling material.[13], [14]

## 24.2.1 METALLURGICAL PROCESSING

### 24.2.1.1 REDUCTION OF THE SILICA FOR THE PRODUCTION OF METALLURGICAL-GRADE SILICON METAL

Metallurgical-grade silicon metal is produced industrially by carbothermic reduction of silicon dioxide in submerged-arc electric furnaces. The input materials include silicon source (such as quartz) and reductant blend comprising coke, coal, charcoal and wood chips. To avoiding introducing too much impurities into the final product high quality silicon source containing >99.5% $SiO_2$ and low-ash-bearing reductant are used. The produced metallurgical-grade silicon typically contains 98.5–99.5% silicon. The common impurities in metallurgical-grade silicon include carbon, alkali-earth and transition metals, as well as boron and phosphorus. The by-product of this silicon metal production process is mainly condensed silica fume (0.2 to 0.4 ton of silica fume per ton of silicon metal).

The overall reaction of the process is shown as follows.

$SiO2 + 2C = Si + 2CO$
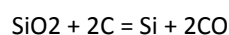
To have the process run properly, high operation temperature is needed (above 1800 °C), thus the process requires a lot of energy, which is supplied by the three electrodes deeply submerged in the charge mix. The specific electric energy consumption for process is 11–13 MWh/ton of silicon metal.

An illustration of the industrial production of silicon metal is shown in **Figure 22**. The raw materials are charged from the top of the furnace and consumed both on the way down and in the craters where the main silicon production occurs. This creates sinks in the furnace top which have to be refilled with new raw materials. During the operation, off gases are generated and collected by hood. The off gases contain a lot of energy, which can be recovered by heat exchangers. The dust in the off gases is filtered through bag house filters and silica fume is collected and be sold as a valuable product to the refractory industry, the oil industry or as an additive in cement. The remaining gas components such as $CO_2$, $SO_2$ and $NO_x$, etc. are released to the air.

Tapping of the furnace is done through tap holes located at the bottom of the furnace. The silicon metal is usually tapped into ladles where it may undergo some form of refining by using oxidative gas and slag-forming additives, mainly silica sand ($SiO_2$) and lime/limestone ($CaO/CaCO_3$). After completion of oxidative refining in the ladle, the slag, which contains part of the impurities, is removed mechanically or by gravity and the liquid silicon is poured into a casting mold. The metal is thereafter transported for crushing, screening and packing before it is shipped out to customers. [7], [12]–[16]
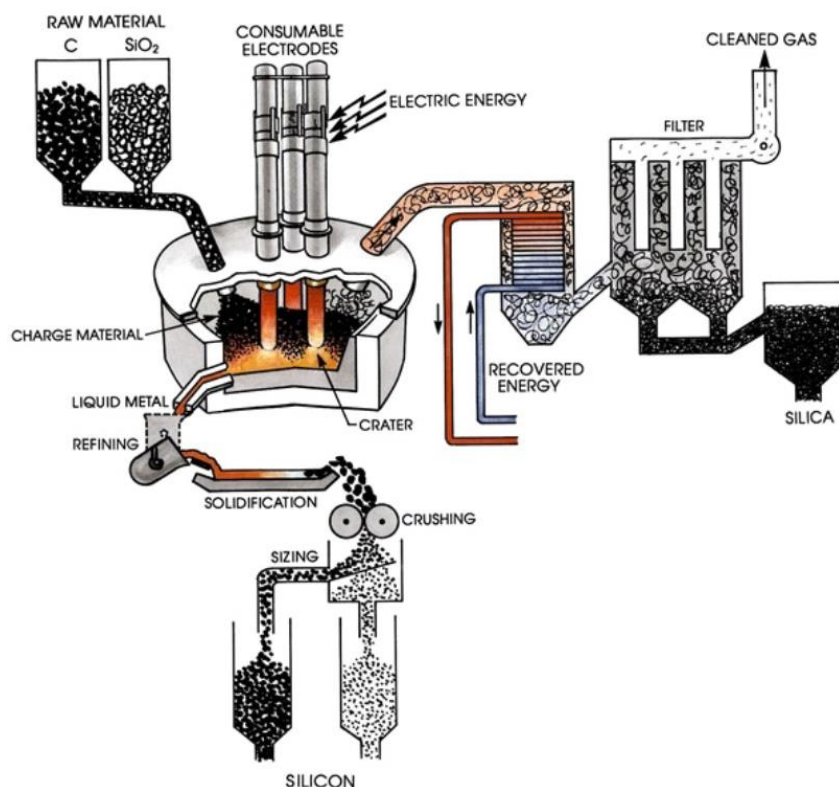
**Figure 22** Industrial production of silicon metal.[12]

## 24.2.1.2     PRODUCTION OF SILICONES AND SILANES

(1)  Silicone production

Silicone is produced from silicon metal. The production process includes a three-step synthesis, namely, chlorosilane synthesis, chlorosilane hydrolysis and polymerisation & polycondensation. An illustration of the silicone production process is shown in **Figure 23** and the description of the process is detailed in [17].
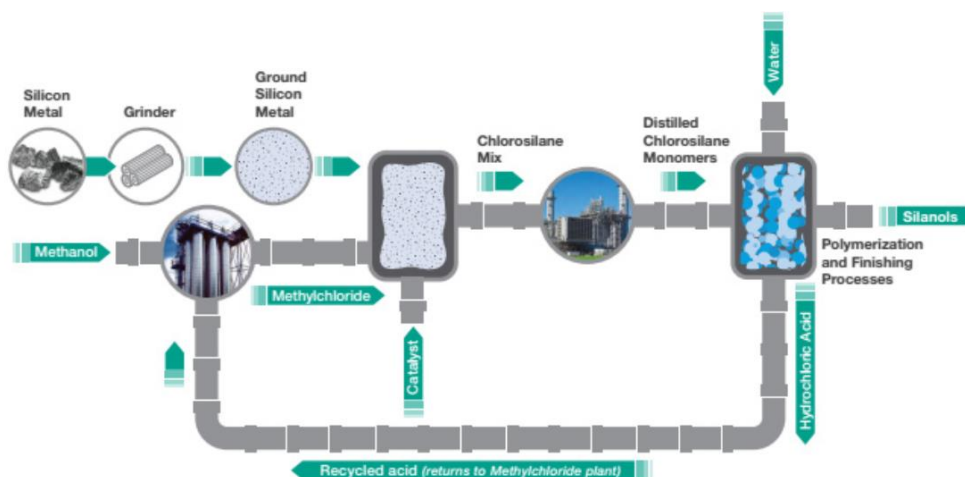


**Figure 23** Silicone Manufacturing Process.[18]

(2) Silanes production

Silanes are a series of compounds made up of silicon and hydrogen. Among the silanes, silane (SiH4) is widely used one. There are several routes to produce silane. The commonly used routes in the commercial scales include: (i) lithium hydride with silicon tetrachloride; (ii) lithium hydride with trichlorosilane; (iii) magnesium silicide with mineral acides and catalytic redistribution of chlorosilanes.[19]

## 24.2.1.3    PRODUCTION OF SILICON-CONTAINING ALUMINUM ALLOYS

Silicon-containing aluminum alloys are produced by adding metallurgical grade silicon metal into the melting furnace, such as induction furnace.

## 24.2.1.4    PRODUCTION OF SOLAR-GRADE AND ELECTRONIC-GRADE SILICON

Metallurgical-grade silicon is the precursor for the production of solar-grade silicon. As seen in **Table 9**, the purity of the solar-grade silicon and electronic-grade silicon are very high. Therefore, the key of the process for the production of solar-grade and electronic-grade silicon is the refining step to remove the impurities from the metallurgical-grade silicon.

The process for the production of solar-grade silicon and electronic-grade silicon can be divided into the chemical route (known as Siemens process) and the metallurgical route. The descriptions of the two processes are shown as follows.

(1) Chemical route
- The Siemens process[7], [12], [20]

The Siemens process is the dominant process for the production of polysilicon. The process contains the following steps:

(i)     The metallurgical-grade silicon particles are fluidized with hydrochloric acid in the presence of catalyst via the reaction Si + 3HCl = SiHCl3 + H2 to form trichlorosilane ($SiHCl_3$) gas;

(ii)    The trichlorosilane undergoes multiple fractional distillation to produce high-grade trichlorosilane.

(iii)   The purified trichlorosilane is reduced by hydrogen via reaction $SiHCl_3 + H_2 = Si + 3HCl$ in a Siemens reactor.

(iv)    Silicon is deposited in a fine-grained polycrystalline form on an electrically heated inverse U-shape silicon rod (T > 1100$^o$C) in a cooled Siemens reactor.

The flow sheet and illustration of the Siemens process are shown in **Figure 24** (a) and (b), respectively.

The main disadvantages of the Siemens process include: (i) the production of chlorosilanes and reactions with hydrochloric acid which is toxic and corrosive; (ii) high energy consumption (200 kWh/kg Si).
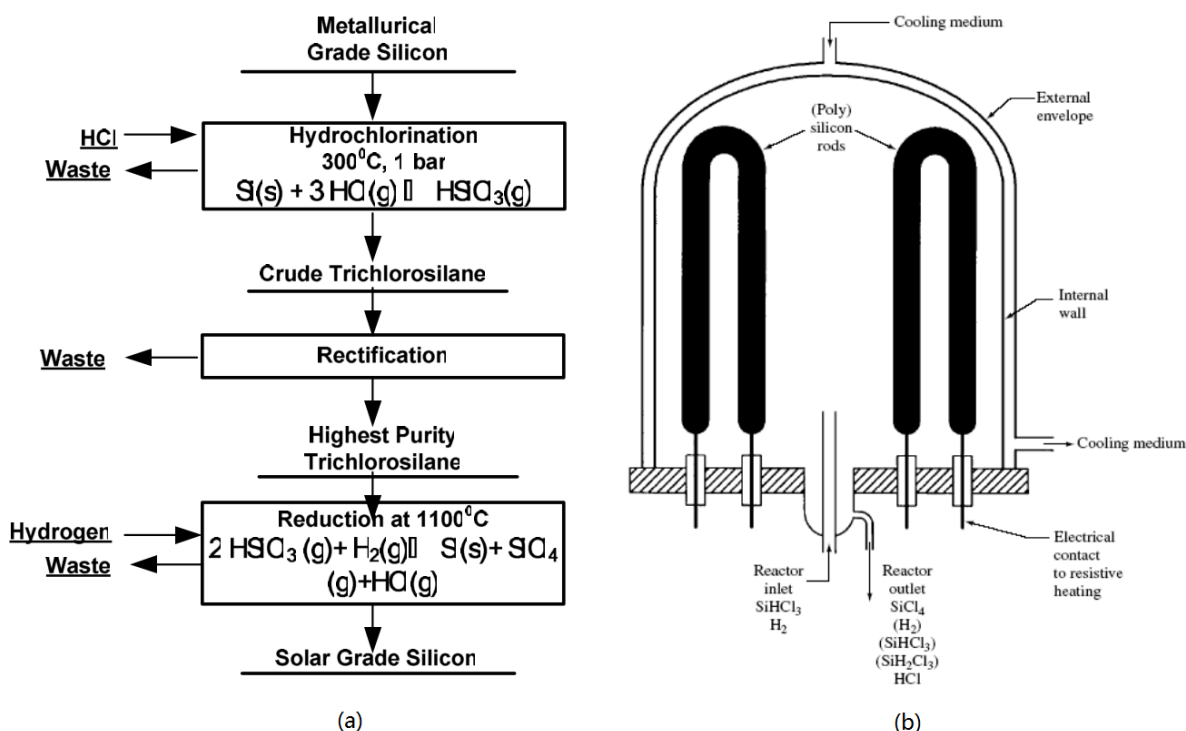
Figure 24 (a) Flow sheet of the Siemens process;[20] (b) Illustration of the Siemens process.[7]

- The fluidized bed process[7], [12], [21], [22]

In the fluidized bed process the highly volatile silane (SiH4) is used instead of the trichlorosilane (SiHCl3). In this process the silicon seeds are fed into the fluidized bed reactor from the top and heated by some means in the reactor. The fluidizing gas (such as hydrogen and helium) and the reactant gas (silane) are injected from the bottom of the reactor to fluidize the particles. In the reactor the silane decompose according to the reaction SiH4 = Si + 2H2. Upon decomposition the silicon is deposited on the particles thus making them grow. After dwelling for a while the particles grow to a size suitable for extraction. The finished beads are then extracted and new small particles can be charged into the reactor as seeds. An illustration of the fluidized bed process is shown in **Figure 25**.

The fluidized bed process has significant advantages compared to the Siemens process, as most of the shortcomings identified for the Siemens process are eliminated. The disadvantages of the process lie in the generation of powder-form polysilicon and the hydrogen adsorption into the materials. Both the Siemens process and the fluidized bed process can produce the silicon with the purity of 99.99999% for the solar and electronic applications. The production share by the Siemens process and the fluidized bed process were about 78% and 16%, respectively, in 2008. It is likely that the fluidized bed process will become the dominating process for the production of solar- and electronic-grade silicon.
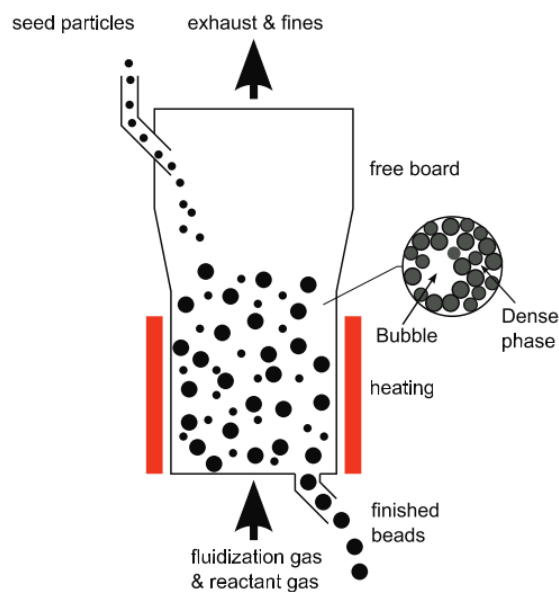
Fig. 2. The fluidized bed reactor.

**Figure 25** Illustration of the fluidized bed reactor for polysilicon production.[21]

(2) Metallurgical route

The metallurgical route entails refining of the metallurgical-grade silicon via several refining steps. Several examples of the refining steps are shown as follows:

(a) Directional solidification and acid leaching to remove the elements (such as Fe, Al, Mg, Sb, Sn, Zn, Cu, Ni and Ti) that have low effective partition ratios in silicon. These elements are highly soluble in molten silicon but their solubility in solid silicon is relatively low. During the solidification the impurities are rejected in the grain boundaries. After crushing and acid leaching the impurities dissolve in the acid and thus the silicon is refined.

(b) Vacuum refining to remove the phosphorus.

(c) Slag refining or plasma refining to remove the baron, carbon and oxygen.

Since certain refining step is only effective to remove specific impurities, combination of the refining steps is required for the refining. Further, using the high-purity metallurgical-grade silicon is preferable for the process. The production share of solar-grade silicon by the metallurgical route was less than 8% in 2008. It is estimated that the production share of silicon by metallurgical route is likely to increase in the future.

## 24.2.1.5   PRODUCTION OF CRYSTALLINE WAFERS

The crystalline wafers are produced from the high-purity silicon. The production can be achieved either by ribbon growth or a two-step process starting with ingot casting or crystallization followed by wafer manufacturing. At moment the production crystalline wafers is overwhelmingly by the latter process, which is described as follows.[12]

(1) Ingot casting

The product from the ingot casting process can be either a mono-crystalline silicon ingot or the poly-crystalline silicon ingot. Poly-crystalline silicon ingot has cost benefit over mono-crystalline silicon ingot; however, mono-

crystalline silicon ingot has less defects and high quality, thus can be used for manufacturing electronics and high-efficiency solar cells.

(a) The Czochralski process for single crystal ingot[12], [23]

The Czochralski process is the common process for the production of crystal ingot. In this process the polysilicon together with boron (B) and phosphorous (P) is melted under vacuum in the quartz crucible at around 1420℃. The crystalline silicon seed rod is placed on the surface of the molten silicon in the crucible, and is pulled up while rotating it to form a monocrystalline ingot, which has the same orientation of atoms as the seed crystal. The Czochralski process is a batch-based process and it takes about two days to complete a production cycle of an ingot. An illustration of the Czochralski process is shown in **Figure 26**.
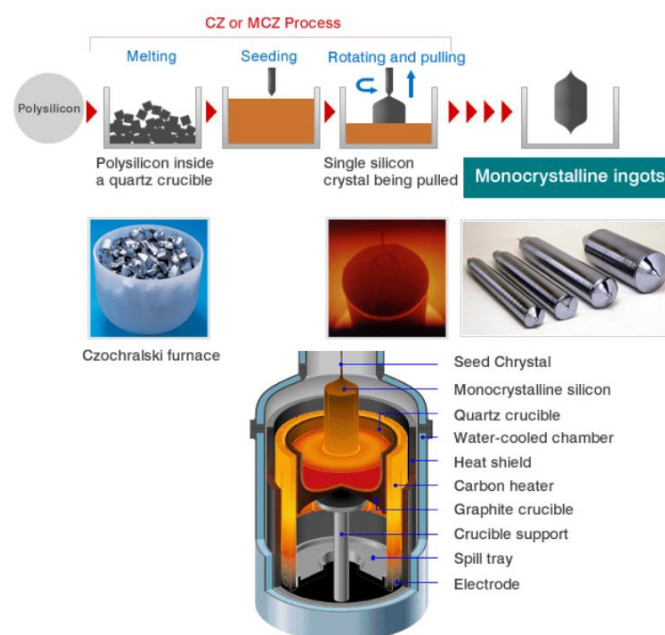


**Figure 26** Illustration of the Czochralski process for the production of monocrystalline ingot.[23]

(b) Bridgman process for polycrystalline silicon ingot[7], [12]

In the case of the Bridgman process, a silicon nitride (Si3N4)-coated quartz crucible is usually employed for melting of the solar-grade or polycrystalline silicon material in a crucible and subsequent solidification of the multi-crystalline ingot. The Si3N4 coating serves as an anti-sticking layer preventing the adhesion of the silicon ingot to the quartz crucible walls. During this process the temperature gradient and growth rate are controlled to favor the growth of a high-quality crystal structure with low thermal stresses. During the solidification refining can also be achieved, as metal impurities are pushed to the top of the ingot. By applying this process the high-quality multicrystalline silicon ingots with mass of 250-300 kg, dimensions of up to $70 \times 70$ cm$^2$ and heights of more than 30 cm can be obtained.

(2) Wafer manufacturing[12]

Prior to wafer manufacturing, the ingots undergo sectioning where the peripheral sections are cut. The mono-crystalline cylindrical ingots undergo sectioning such that cubic ingots are produced, while multi-crystalline ingots are sectioned for the removal of highly contaminated peripheral regions. The ingots are then cut to blocks with a cross-sectional area (eg. 15.6 x 15.6 cm$^2$) equal to the wafer size. About 25% and 15% of the material is lost from cutting of the mono-crystalline and multi-crystalline ingots respectively.

Wafers are produced by cutting the silicon blocks into pieces with a thickness of less than 200 microns by using the muti-wire saw machines. During the cutting approximately 30% of the silicon is wasted as saw dust.

## 24.3 VALUE CHAIN, IDENTIFICATION OF SECONDARY RESOURCES AND LOSS INTO THE ENVIRONMENT

According to the primary flow of the silicon metal, the primary value chain of the silicon metal can be drawn, as shown in **Figure 27**, in which the secondary resources of silicon metal and the loss of silicon into the environment and other materials can be identified.

(4) Fines generated during the mineral processing. The fines are an important residual material; however, it cannot be used for producing silicon metal.

(5) Silica fume. Silica fume (0.2-0.4 ton of silica fume per ton of silicon metal) is an important residual material generated during the sub-merged arc furnace processing of quart/quartzite into silicon metal. This residual material is normally used as purposes other than for producing silicon metal.

(6) Other residues from the production processes. Various types of residuals are generated during the production and manufacturing processes of silicon metal. However, it is believed that they are rarely used except certain types that have similar properties as silicon metal. The two types of residual materials of this kind are cut-off residuals from the silicon ingots and the sludge during the cutting of ingots).

(7) End-of-life products. End-of-life products from silicon-containing aluminum alloys and solar products can be possibly used to recover silicon. However, it is believed that a part of silicon is lost to the environment or other materials due to discard and dilution.
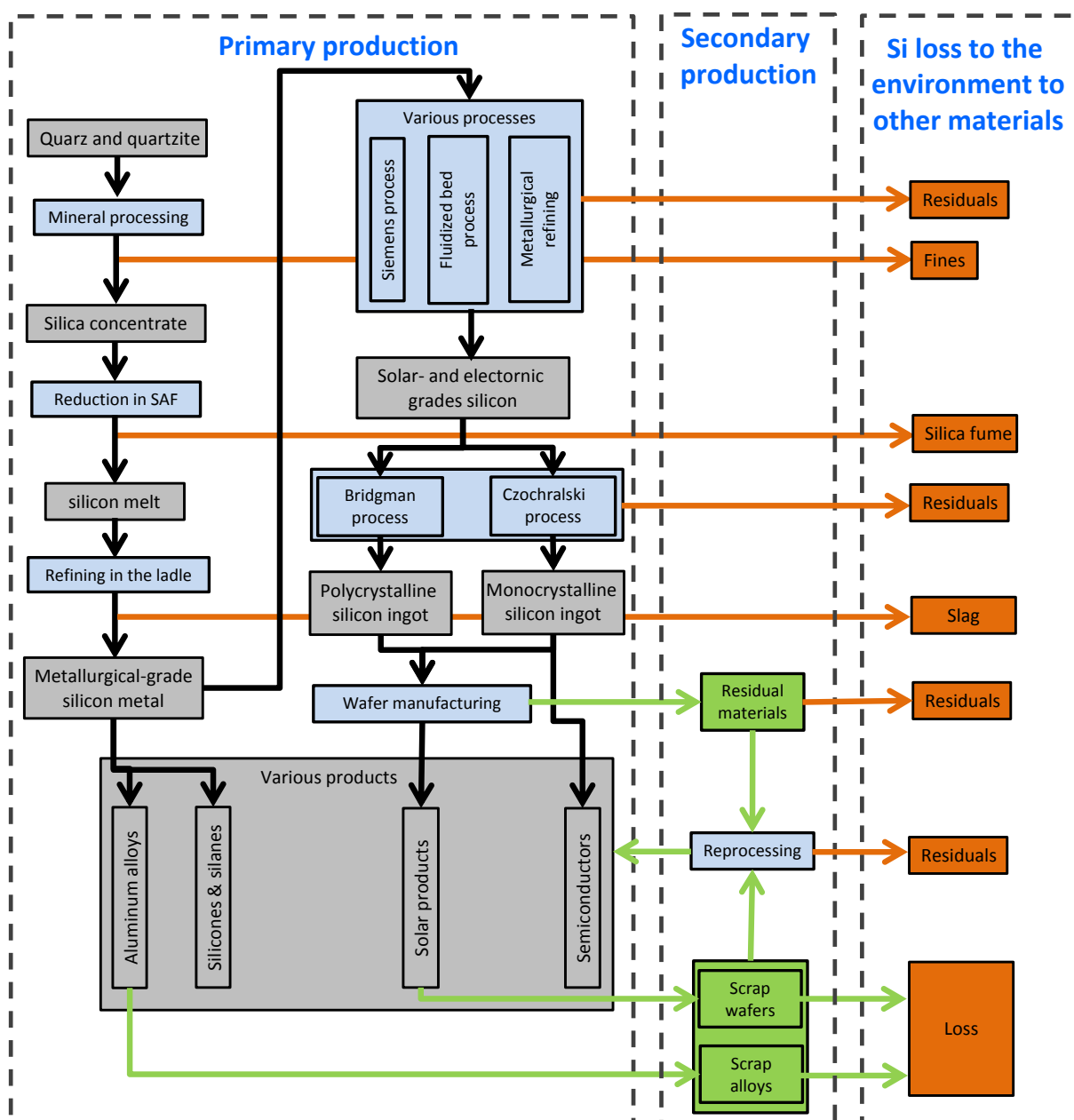
**Figure 27** Value chain of silicon metal.

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## 25 TANTALUM

### 25.1 PRODUCTION LINES OF IDENTIFICATION FROM PRIMARY RESOURCES

Tantalum is a chemical element with the atomic number of 73. It is a part of refractory group metals which are widely used for alloys. The common occurrence is in minerals like tantalite, columbite and coltan (a mixture of columbite and tantalite).

### 25.1.1 WORLD PRODUCTION AND RESERVES

Important tantalum resources have been identified to be contained in tantalum minerals in: Brazil 38%, Rwanda 25%, Australia 8%, Canada 8% and othr sources cca 2%.

Tantalum metal resources have been identified to be in: China 19%, Indonesia 10%, Kazakhstan 9%, Austria 9% and other countries cca 53%.

Tantalum waste and scrap: Indonesia 19%, Austria 19%, China 14% and other 50%.

The total imports were: China 37%, Kazakhstan 25%, Germany 14%, Thailand 12% and other 12%.

Table 1. The tantalum world production and reserves as of January 2017

| Country | Production – All forms | | Reserves |
|---|---|---|---|
| | 2015 | 2016 | |
| United States | - | - | - |
| Australia | - | - | 62000 |
| Brazil | 140 | 140 | 36000 |
| Burundi | 33 | 30 | NA |
| Canada | 50 | 50 | NA |
| Congo (Kinsasha) | 100 | 110 | NA |
| Ethiopia | 95 | 10 | NA |
| Mozambique | 39 | 40 | NA |
| Nigeria | 63 | 60 | NA |
| Rwanda | 150 | 150 | NA |
| World Total (rounded) | 670 | 590 | >100000 |

There are other (natural) identified resources for tantalum in the world: Australia, Brazil and Canada, which are considered to meet the need of the consumption in the world. US has about 1500 tons of tantalum resources which were/are considered uneconomical to exploit due to the current low prices.
Tantalum can be extracted together with Niobium, thus can be counted as a possible secondary product from niobium mining.

### 25.1.2 MAJOR USES

Major uses of tantalum are in tantalum capacitors mostly for automotive capacitors, mobile phones and personal computers. Tantalum oxide ($Ta_2O_5$) is used in glass lenses, for making them more flexible and lighter, as well as to improve the sharpness. Tantalum carbide is used in cutting tools.
The value of the consumed tantalum in 2016 has been estimated to be around 290 million US dollars.

### 25.1.3 RECYCLING

Tantalum is recycled especially from electronic waste. There is no readily available numbers on the quantities produced this way.

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## 26.1 PRODUCTION LINES OF IDENTIFICATION FROM PRIMARY RESOURCES

### 26.1.1 W, PRODUCTION AND APPLICATIONS

Tungsten, also known as wolfram, with symbol W and atomic number 74, has the highest melting point of all metals (3,422± 15°C). With its density of 19.25g/cm3, tungsten is also among the heaviest metals. Tungsten features the lowest vapour pressure of all metals, very high moduli of compression and elasticity, very high thermal creep resistance and high thermal and electrical conductivity. Tungsten is the most important metal for thermo-emission applications, not only because of its high electron emissivity (which is caused by additions of foreign elements) but also because of its high thermal and chemical stability. It usually contains small concentrations of carbon and oxygen, which give tungsten considerable hardness and brittleness (ITIA).

Cemented carbides, also called hardmetals, are the most important usage of tungsten today. Tungsten monocarbide (WC) is the main constituent which has hardness close to diamond. Hardmetal tools are applied for the shaping of metals, alloys, ceramics and other materials. About 54% to 72% of tungsten in the world are used for hardmetals. Steel and alloys, mill products such as lighting filaments, electrodes, electrical and electronic contacts, wires, sheets, rods etc., and a widespread variety of chemicals are other important uses of tungsten.

With very high economic importance and high supply risk tungsten was listed as one of the 20 critical materials in Europe (EC, 2014). The world production of tungsten concentrate is distributed over a quite large number of countries but over 80% of it produced in China. According to the USGS 2016 report the world total mine production of tungsten in 2015 was 87, 000 t and 71,000 t was from China. Currently, four EU countries including Austria, Portugal, Spain and UK are producing tungsten concentrate and totally 2,830 t of tungsten was produced in 2015. The consumption of tungsten in EU is about 10,000 t per year which was predicted to keep slightly increase in the future 10 years (H.C.Starck, 2013). Therefore, increasing the production of tungsten from primary resources should be one of important pathways to satisfy the demand of the metal in the EU market.

### 26.1.2 PRIMARY RESOURCES FOR W PRODUCTION

Average abundance of tungsten in the earth's crust is estimated to be 1.25-1.5 ppm, about the same as tin and molybdenum. It is more abundant in granite (about 2 ppm) than basaltic (1 ppm) and ultra-mafic rocks (0.5 ppm). There are numerous tungsten minerals, but only scheelite ($CaWO_4$) and wolframite (($Fe, Mn)WO_4$) the intermediate between ferberite ($FeWO_4$) and hübnerite ($MnWO_4$) are of economic importance. Scheelite and wolframite are rather stable with respect to chemical weathering (Schmidt et al., 2012; BGS, 2011).

The world reserves of tungsten are estimately 4.000.000 t W of which China holds about 40 % (Bernhart, 2015). Five major types of tungsten ore deposits are skarn, vein/stockwork, porphyry, disseminated or greisen, and stratabound (BGS, 2011). Most current production of tungsten are from these deposits. The typical grade (WO3%), tungsten mineral, accompaning minerals and mines of these deposits are shown in Table 1. Other deposit types include pegmatite, placer, brine/evaporate and hot spring.

Table 1 Major types of tungsten ore deposits

| Deposit type | Typical grade, WO$_3$% | Tungsten mineral | Accompanying metals | Mine |
|---|---|---|---|---|
| Skarn (deposit size $<10^4$–$5\times10^7$ t) | 0.3-1.4 | Scheelite | Cu, Mo, Zn and Bi | Cantung (Canada); Los Santos (Spain); Vostok-2 (Russia) |
| Vein/stockwork deposit size $<10^5$–$10^8$ t) | variable | Wolframite | Sn, Cu, Mo, Bi and Au | Pasto Bueno (Peru); Panasqueira (Portugal); San Fix (Spain); Chollja (Bolivia) |
| Porphyry (deposit size $<10^7$–$10^8$) | 0.1-0.4 | Wolframite or/and scheelite | Mo, Bi and Sn | Xingluokeng (China); Yangchuling (China); Northern Dancer (Canada); Climax (USA) |
| Disseminated (deposit size $<10^7$–$10^8$ t) | 0.1-0.5 | wolframite and scheelite | Sn, Bi, Mo | Shizhuyuan (China) |
| Stratabound (deposit size $<10^6$–$10^7$ t) | 0.2-1.0 | Scheelite | | Mittersill (Austria); Damingshan (China); Mount Mulgine (Australia) |

As the largest producer of tungsten in the world China has more than ten super large tungsten mines annual output over 1300 tonnes of WO3. Most of them are located in Jiangxi and Hunan, the south of China. The Xianglushan located in Jiangxi is the largest tungsten mine in China with the annual output of over 5700 tonnes of WO3. The Shizhuyuan located in Hunan is a large polymetallic tungsten mine with the annual output of 5500 tonnes of WO3. It is a W-Sn-Mo-Bi polymetallic deposit and characterized by low grade and complicated composition (Han et al., 2017). The ore contains scheelite, wolframite, molybdenite, cassiterite, bismuthinite, and fluorite. The Nui Phao mine based in Vietnam is the largest tungsten mine outside of China and an unique polymetallic mine with significant deposits of tungsten, fluorspar, bismuth and copper. The mining reserves are 66 million tonnes of ore with average grade 0.21% WO3 (Masan Resources, 2012). The Vostok-2 is Russia's largest skarn deposit of high grade sulfide–scheelite ore with substantial base metal and gold mineralization. It has been mined since 1969 first in open pit, and subsequently by means of underground mining operations (Soloviev and Krivoshchekov, 2011). The Cantung mine located in western Northwest Territories of Canada is a skarn type of deposit with the reserves of 1.8 million tonnes at the grade 0.81 % WO3. It is continuously operating underground and seasonally operating in open pit.

The Mittersill mine in Austria hosts the largest tungsten deposit in Europe producing scheelite concentrates. The deposit consists of two parts, the Ostfeld open pit mine and the Westfeld underground mine (Thalhammer et al., 2008; Holzer and Stumpfl, 1980). The Los Santos mine is an open pit scheelite skarn deposit located in western Spain with the reserves 3.58 million tonnes at average grade 0.23% WO3. It was originally opened in 2008 according to the report of Almonty Industries (Wheeler, 2015). The Barruecopardo tungsten project situated in Spain is planned to be an open pit operation and one of the biggest tungsten projects in Europe. Tungsten mineralisation is found in quartz veins mostly in the form of coarse grained scheelites less than 10cm

in thickness with minor traces of wolframite (http://www.mining technology.com/projects/barruecopardo-tungsten-project-castilla-y-leon/). The Panasqueira mine is Portugal's largest tungsten-producing mine with the reserves of 4.91 million tonnes of ore at 0.22% WO3 mined in underground methods. Hemerdon tungsten mine situated in Devon England was opened in 2015. The deposit hosts 35.7 million tonnes of ore at 0.18% WO3 in wolframite and 0.03% Sn mined in open pit methods. The mineralisation includes an oxide-silicate stage consisting of wolframite, cassiterite, arsenopyrite, topaz, muscovite and tourmaline.

## 26.2 PROCESSING TECHNIQUES RECOGNITION AND ANALYSIS

### 26.2.1 MINERAL PROCESSING

The beneficiation process of scheelite and wolframite ores generally consists of pre-concentration after crushing and grinding, followed by roughing, cleaning and final purification stages to produce a concentrate with 65-75% WO3 fulfilling the requirements of international trading (Krishna, 1996; Lassner and Schubert, 1998). Only scheelite is readily amenable to flotation. Wolframite, in contrast to scheelite, is paramagnetic. Thus beneficiation techniques of gravity concentration and flotation are applied for scheelite ore, and gravity and/or magnetic separation applied for wolframite ore.

Due to the brittle character of both scheelite and wolframite, comminution is carefully designed to avoid overgrinding, that is, at every stage of comminution, appropriate sizing techniques (screening, hydro-classifications by using hydrocyclones or classifiers), are used to minimise formation of fines, and rod milling is more commonly used than ball milling. X-ray sorting and gravitational methods are normally used for the pre-concentration and optical sorting and/or hand-picking methods are also used for the pre-concentration of wolframite ore in operations. The high density of both scheelite and wolframite facilitates their separation from the gangue minerals by gravity techniques. Jigs, spirals, shaking tables and centrifugal concentrators (the Knelson, Kelsey and Falcon concentrators) are usually used in operations in wide range of particle size.

Normally, two concentration flowsheets are used for scheelite ore flotation: 1) whole ore flotation after pre-concentration and; 2) gravity-flotation flowsheet. Gravity concentration is to remove the low-density fraction (e.g. calcite, fluorite etc.) before flotation of scheelite. Scheelite flotation is performed in alkaline medium, with sodium carbonate or sodium hydroxide to adjust the pH to about 9 - 10.5. The most important collectors are fatty acids such as oleic acid, linoleic acid and palmitic acid (Bernhart, 2015), and sodium oleate, tall oil or oxidized paraffin soap (Han et al., 2017). In the case of the Petrov process, which is normally applied for further separation of scheelite from other calcium minerals, flotation with fatty acids is undertaken at elevated temperatures which increase the selectivity between scheelite and other Ca-bearing minerals. In China, higher temperatures are used in the cleaner flotation, together with using depressants (e.g. sodium silicate) for effective depression of Ca-bearing minerals other than scheelite. Besides sodium silicate, phosphates and organic compounds such as starch, quebracho and tannic acid have also been used as modifiers in scheelite flotation (Li and Li, 1983). The beneficiation flowsheet of tungsten minerals (scheelite and wolframite) in Shizhuyuan mine is shown in Figure 1 (Han et al., 2017).
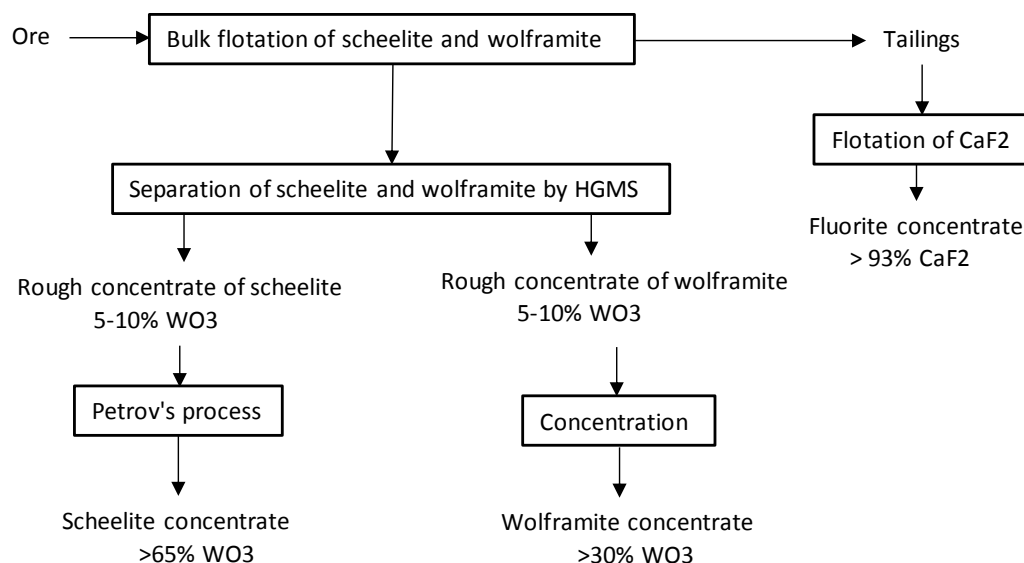
Fig.1. Beneficiation flowsheet of tungsten minerals (scheelite and wolframite) in Shizhuyuan mine

Flotation is rarely applied to wolframite ore since it occurs mainly in much coarser mineralization with then a preference to gravity and magnetic methods (Lassner and Schubert, 1998). But for fine-grained and complex wolframite ores flotation becomes an effective method for recovery of fine wolframite (Pradip, 1996; Meng, Q. et al., 2015; Ai et al., 2017a). Wolframite flotation is performed similarly to the scheelite flotation, but is not pH sensitive and can therefore be undertaken in both acidic and alkaline solutions.

Low-intensity magnetic separation (LIMS) is used to remove magnetite and other ferromagnetic materials. Magnetizing roast might also be used for transforming hematite into magnetite prior to LIMS. High intensity magnetic separation (HIMS) is used to separate wolframite from diamagnetic minerals such as cassiterite. Industrial applications of magnetic separations for scheelite ore concentration are rare but high gradient magnetic separation (HGMS) is used for scheelite - wolframite separation at the Shizhuyuan mine in China (Han et al., 2017).

Electrodynamic or electrostatic separators are used for scheelite-cassiterite separation as scheelite is non-conducting whereas cassiterite is a conducting material (Lassner and Schubert, 1998). Acid leaching can be performed to remove apatite and calcite (Li and Li, 1983). For example, the process implemented at the Salau mine (France, closed in 1986) HNO3 was used to remove the apatite and carbonates contained in the scheelite concentrate after flotation.

Tungsten ore can contain a wide range of minerals associated with scheelite and/or wolframite. The international specifications for the chemical composition (in %) of scheelite and wolframite concentrates (BGR, 2010) are shown in Table 2.

Table 2 International specifications for the chemical composition (in %) of scheelite and wolframite concentrates

|  | Wolframite | | | Scheelite | | |
|---|---|---|---|---|---|---|
|  | General | Grade I | Grade II | General | Grade I | Grade II |
| WO3 | 65.00-70.00 | >=65 | 60-64.99 | 60.00-70.00 | >=70 | 65-69.99[1] |
| Sn | 1.00-1.50 | 0.20-1.00 | <=2.5 | <=0.1 | | |
| As | 0.10-0.25 | <=0.20 | <=0.40 | <=0.10 | <=0.3 | |
| Cu | <=0.10 | 0.08-0.40 | <=1.0 | <=0.10 | - | |

| | | | | | | |
|---|---|---|---|---|---|---|
| Mo | 0.04-0.40 | <=0.40 | <=1.0 | 0.05-0.40 | <=2.0 | <=4.0 |
| P | 0.05-0.10 | 0.03-0.08 | <=0.25 | 0.05-0.10 | <=0.1 | |
| S | 0.10-0.50 | 0.20-0.75 | <=2.0 | <=0.5 | | |
| Bi | <=1.00 | | | 0.05-1.00 | | |
| Sb | <=0.50 | - | | <=0.05 | <=0.2 | |
| Mn | 0.00 | | | <=1.00 | | |

[1] Lower grade scheelite ores are usually converted into artificial scheelite direct at the mine or later into ammonium paratungstate, an important intermediate product of the synthesis of tungsten.

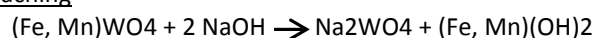
## 26.2.2 METALLURGICAL PROCESSING

### HYDROMETALLURGY

The hydrometallurgical recovery of tungsten from various sources (e.g. minerals, tailings, scrap) follows several process steps. After digestion and purification of the raw material, the concentrated leachates enter the solvent extraction cycle to produce high-purity ammonium paratungstate (APT), which is the most important intermediate for pure tungsten production (MSP-REFRAM D2.2, 2016).

**Digestion**
Tungsten is economically extractable from the two minerals wolframite ($(Fe, Mn)WO_4$) and scheelite ($CaWO_4$) and from tungsten containing scrap (e.g. catalysts). There are three hydrometallurgical routes for processing the tungsten bearing raw materials:
Alkali leaching
$$(Fe, Mn)WO_4 + 2\ NaOH \rightarrow Na_2WO_4 + (Fe, Mn)(OH)_2$$
The wolframite or oxidized soft scrap is dissolved in concentrated NaOH (40 – 50 %) at 100 – 150 °C or by high-pressure digestion with dilute NaOH. Fe and Mn build low soluble hydroxides.
Pressure leaching with soda
$$(Fe, Mn)WO_4 + Na_2CO_3 \rightarrow Na_2WO_4 + (Fe, Mn)CO_3$$
$$CaWO_4 + Na_2CO_3 \rightarrow Na_2WO_4 + CaCO_3$$
The wolframite or scheelite is leached with $Na_2CO_3$ (10 – 18 %) under pressure (10 – 25 bar) in steel autoclaves at 200 °C. A large excess of reagent is necessary.
Acid leaching
$$CaWO_4 + 2\ HCl \rightarrow CaCl_2 + H_2WO_4$$
The scheelite is leached with concentrated HCl, but other acids are also possible. The precipitated tungstic acid is filtrated from the aqueous $CaCl_2$ solution and treated with ammonia and water to produce APT.
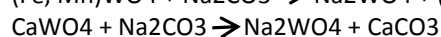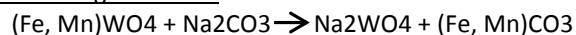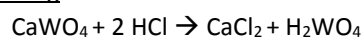
**Purification**
The obtained sodium tungstate solutions from alkali and soda leaching need to be purified by filtration and precipitation, because they may contain several dissolved impurity elements. If the concentration of those impurities is too high, the subsequent processing is disturbed.
Silicates are common impurities, which can be precipitated by aluminium sulfate or magnesium sulfate solution (or a mixture) at pH 8 – 11. Phosphates and fluorides are co-precipitated.
Molybdenum as a common accompanying element in tungsten bearing material is precipitated by sodium sulfide in neutral or slightly alkaline environment forming thiomolybdate. By adding sulfuric acid to pH 2.5 – 3 the molybdenum is precipitated as trisulfide. This precipitation step is also selective for other insoluble sulfides as As, Sb, Bi, Pb, and Co.

The sodium ion concentration must be reduced from 70 g/l to < 10 mg/l as otherwise problems occur with the reduction to metal powder. This purification step is accompanied by a concentration step of tungsten, which is either done by solvent extraction or ion exchange resins.

**Solvent extraction**

The purified acidic sodium tungstate solution (pH 2 – 3) is contacted with the organic phase. Tertiary or secondary aliphatic amines (e.g. trioctylamine, tricaprylamine) are the most important extractants, unless in literature, various other extractants have been tested. The extractants are dissolved in kerosene or other aliphatic solvents. Phase modifiers like isodecanol can be added. The anionic exchange mechanism writes as follows:

$$\left[W_xO_yH_z\right]^{n-} + \overline{nX\,HY} \rightleftarrows \overline{(X\,H)_nW_xO_yH_z} + nY^-$$
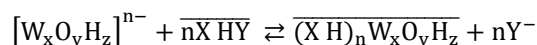
Here X represents the extractant (amine) and Y the anionic leaving group, where the overbars indicate the organic species. The tungsten ionic species is pH-dependent. The predominant aqueous species are $[W_6O_{21}H_3]^{3-}$, $[W_{12}O_{42}H_6]^{6-}$ and $[W_{12}O_{40}H_2]^{6-}$ at pH 2, $[WO_4]^{2-}$ at pH 7 and $[WO_6H_2]^{4-}$ at pH 12. The distribution coefficient at pH 2 is between 30 – 50. Therefore a two-stage countercurrent extraction is sufficient for an extraction of 99.9 %.

The extract is washed with deionized water and reextracted by a dilute ammonia solution into the aqueous phase:

$$\overline{(X\,H)_nW_xO_yH_z} + nOH^- \rightleftarrows \left[W_xO_yH_z\right]^{n-} + \overline{n(XH)(OH)}$$

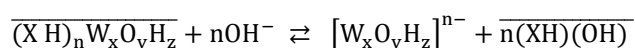The solvent is regenerated and recycled.

**Ion exchange**

Here the sodium tungstate solution is contacted with a strongly alkaline ion exchange resin in the chloride from, where the tungstate is adsorbed. Desorption is carried out with ammonium chloride solution. Elements that form heteropolytungstates like Si, P, As and Mo can additionally be removed.

**Crystallization**

The isopolytungstate solution is evaporated and water and ammonia is distilled, which is recycled to the solvent extraction step. The solubility becomes lower and APT crystallizes in recirculating batch crystallizers. Additionally, this is a further purification step, where soluble impurities remain in the mother liquid.

## PYRO-METALLURGY

As shown in Figure 2 (G. R. Smith, 1994), tungsten concentrates (wolframite or scheelite), obtained after mineral processing of tungsten ore, can be directly used to produce ferrotungsten, steel and tungsten chemicals, or indirectly used to produce tungsten metal powder and tungsten carbide (MSP-REFRAM D2.2, 2016).
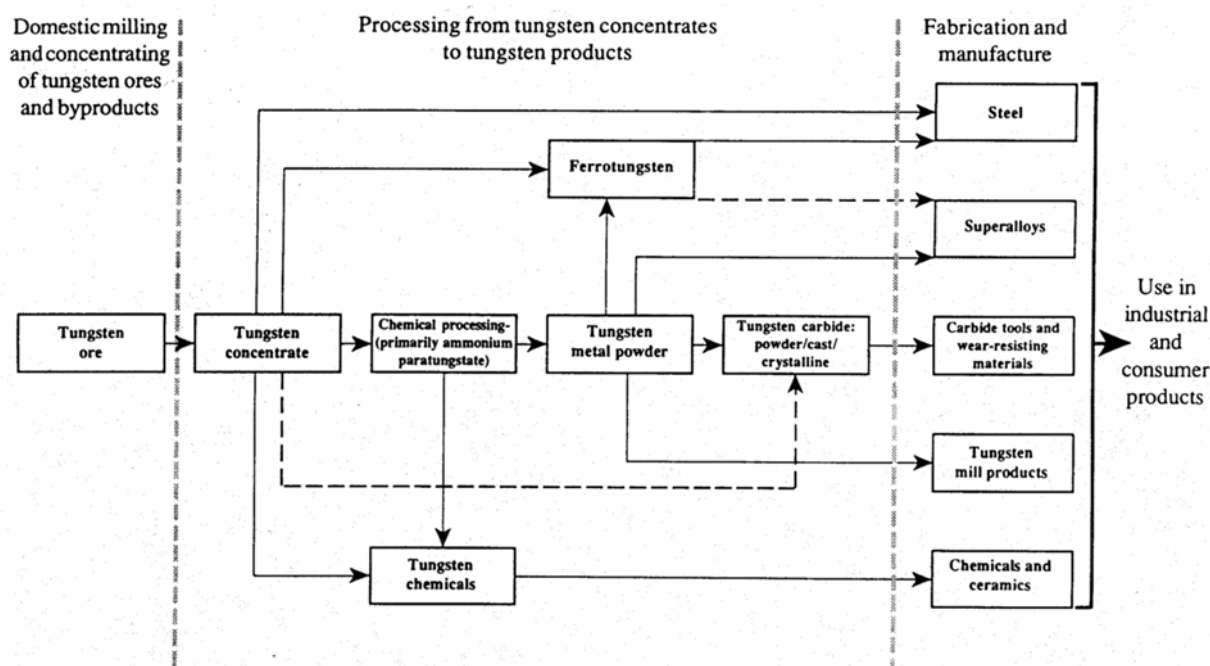
Figure 2 General tungsten flow diagram from primary resources

Using tungsten concentrate to produce ferrotungsten

Ferrotungsten, contains ~ 75-85% W, is a master alloy for the production of tungsten-containing steels. Ferrotungsten is normally produced in the electric arc furnace by either carbo-thermic reduction, carbo-/silico-thermic reduction or alumino-thermic reduction of tungsten concentrates, among which the carbo-thermic reduction and carbo-/silico-thermic reduction are preferred processes due to the cost reasons and the high tolerance level for impurities, such as As and Sn, in the raw materials (Lassner and W.-D. Schubert, 1999; M. Gasik, 2013).

**Carbothermic reduction process.** The carbo-thermic reduction process of tungsten concentrates can be well illustrated by Figure 3 (Lassner and W.-D. Schubert, 1999). It is seen that this process is operated in two stages: the refining stage and the reduction stage. In the refining stage an ingot of high-grade ferrotungsten (80% W) and a $WO_3$-rich slag (25% W) are produced. The ferrotungsten ingot is removed from the furnace and cleaned after the electric arc furnace is switched off, as tapping of the melt is not possible due to a high melting temperature of the ferrotungsten. In the reduction stage the $WO_3$-rich slag is processed to ferrotungsten of 50% W and a slag with less than 1% $WO_3$. The 50% W together with the outer parts of the cleaned, high-grade ingot are recycled and be processed to high-grade ferrotungsten in the refining stage. If several furnaces are used in parallel, the production can then take place as a quasi-continuous process.

Figure 3 Scheme of ferrotungsten production by carbothermic reduction process

**Carbo- and silico-thermic reduction process.** This process is carried out in three successive stages in the electric arc furnace. In the first stage tungsten concentrates are reduced by carbon under $WO_3$ rich slag (10-16% W) and the resulting ferrotungsten (75% W) is s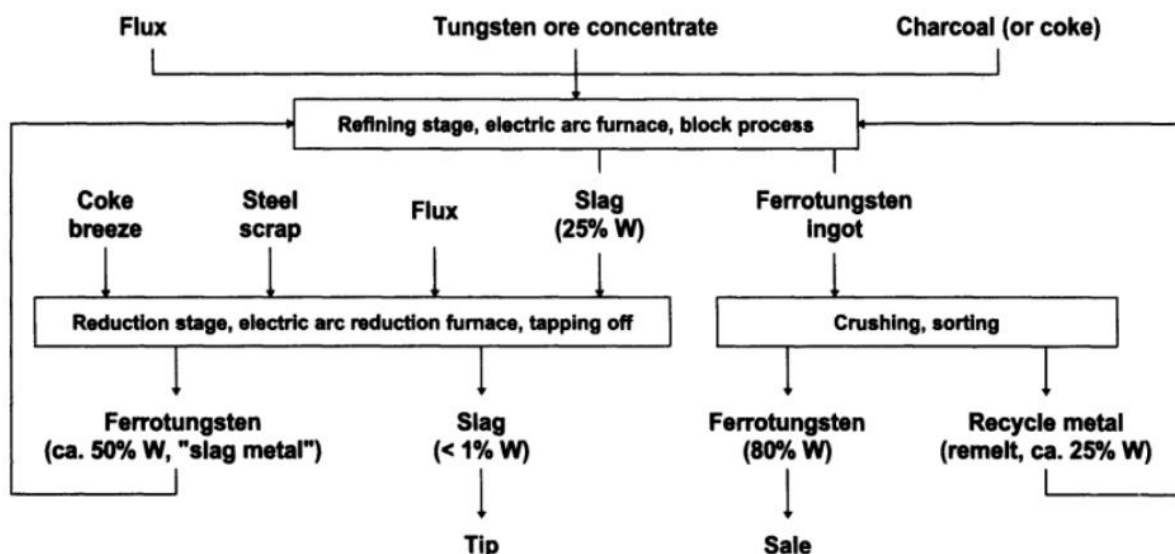cooped out. In the second stage iron scrap is added into the furnace and the $WO_3$-rich slag from the first stage is reduced by silicon (in the form of ferrosilicon with 75% Si), which will result in a metal phase with 50-70% W and a slag phase with < 1% $WO_3$ being tapped off. In the third stage the metal phase in the second stage is refined by adding tungsten concentrates, resulting in a $WO_3$-rich slag (18-25% W) and the W in the metal phase being increased.

Carbo-/silico-thermic reduction process is a continuous operation process, which therefore saves electric energy and prolongs the service time of the lining. However, it necessitates the laborious scooping operation; moreover, ferrotungsten tends to accumulate on the furnace wall, and this can only be removed until next furnace relining.

**Alumino-thermic reduction process.** In this process aluminum is used instead of carbon and/or silicon to reduce the tungsten concentrates, which are mainly scheelite. Due to the chemical properties of aluminum the reduction proceeds rather rapidly and the impurities, such as As and Sn, can also be reduced. Therefore, the tungsten concentrates with fewer impurities are required for this process. The resulting product is low carbon ferrotungsten. Due to the economic reason, this process is mainly used to meet special customer needs.

Using tungsten concentrates to produce W-bearing steels
Besides using ferrotungsten for W-bearing steel production, tungsten concentrates (normally scheelite) can be directly, for example, charged into the EAF, to produce W-bearing steel. (G. R. Smith, 1994; Z. Yong and L. Zhengbang, 2006; International Tungsten Industry Association). In this process tungsten oxides in the concentrates is reduced to tungsten by carbonaceous materials in the furnace and the steel is alloyed with tungsten.

Using tungsten concentrates to produce ammonium paratungstate (APT) and its downstream products (mainly tungsten metal powder and tungsten carbide)
**APT production.** Besides a part of tungsten concentrates are used to produce ferroalloys and steels, tungsten concentrates (~ 90% in amount[43]) are largely used to produce APT, a most common intermediate product used

for tungsten metal powder and tungsten carbide production. APT is produced by the modern hydrometallurgical process (International Tungsten Industry Association; E. Lassner, 1995; R. P. S. Gaur, 2006) which can be well described by Figure 4. In this process tungsten concentrates after roasting or calcination are digested by either soda or concentrated NaOH solution, which will result in the formation of sodium tungstate solution. The sodium tungstate solution is purified by precipitation and filtration, and thereafter it is converted into an ammonium tungstate solution, exclusively by solvent extraction or ion exchange resins. Finally, high purity APT is obtained by crystallization, with the formula $(NH_4)_{10}(H_2W_{12}O_{42}) \cdot 4H_2O$.
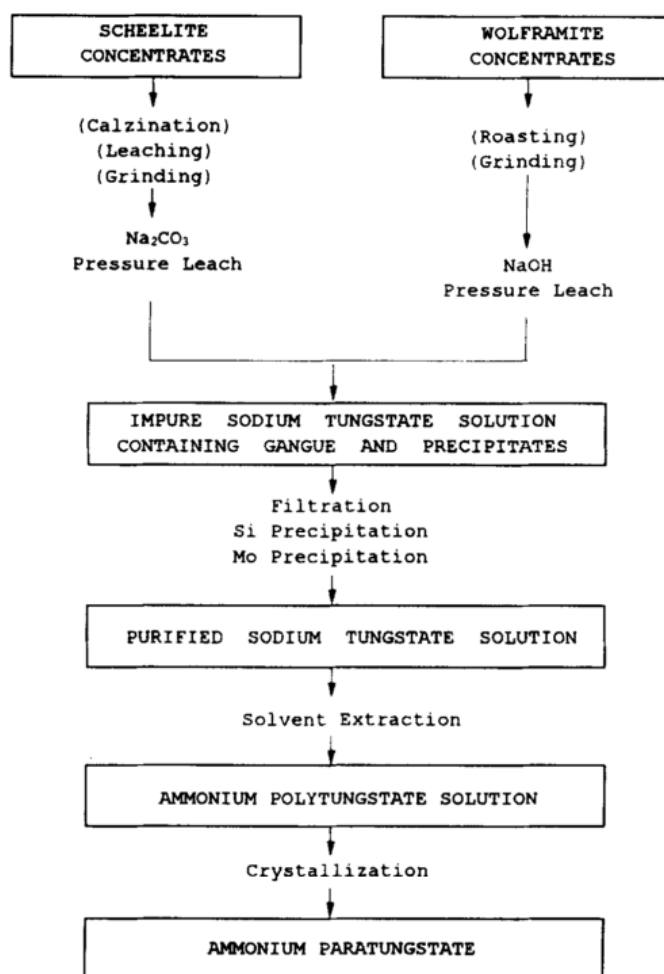


Figure 4 Scheme of APT and $WO_3$ production by modern hydro-metallurgical process

**Tungsten powder production.** Although it is possible to produce tungsten metal powder by direct hydrogen reduction of APT, metal powder is more commonly produced by the hydrogen reduction of tungsten oxide at 600-1000 °C, which is produced by the thermal decomposition of the APT, as shown in Figure 4. By changing reduction conditions this process offers the possibility to produce tungsten powder with various particle sizes (within the range of 0.1-100 μm) (R. P. S. Gaur, 2006; International Tungsten Industry Association; Oleg D. Neikov ET AL., 2009). The other innovative tungsten powder production processes include solid carbon reduction process, gas phase precipitation process, plasma process, amalgam process, carbonyl process, electrochemical reduction process (Oleg D. Neikov ET AL., 2009; D. Tang ET AL., 2012; M. Erdoğan and I. Karakaya, 2010) etc.

**Tungsten carbide powder production.** Conventionally, tungsten carbide is produced by two steps: the step of producing high purity tungsten powder with desired properties and the step of tungsten powder carbonization

by high purity carbon black, soot or graphite. The carbonization step is implemented by (i) mixing the tungsten powder with carbon black, soot or graphite by ball milling and (ii) carbonizing tungsten powder at temperatures of 1400 - 1600°C in hydrogen atmosphere for 2-10 hours. By far a large percentage of WC is manufactured by this direct carburization of tungsten powder process and it covers the widest range of powder qualities in regard to average particle size (0.15–12μm) (International Tungsten Industry Association; R. Koc and S. K. Kodambaka, 2000). The other innovative tungsten powder production processes include direct carbothermic reduction of $WO_3$, scheelite or wolframite (J. Ma and S. G. Zhu, 2010; R. Polini et al., 2016; A. Kumar, 2011) direct carbonization of $WO_3$ by $CH_4$-$H_2$ mixtures (J.M. Giraudon et al., 2000), direct carbothermic reduction of carbon coated $WO_3$ (R. Koc and S. K. Kodambaka, 2000), etc.

An assessment of the extractive technologies for tungsten

Due to the extreme high melting temperature of tungsten, hydrometallurgical process will continue to the prevalent one for extracting tungsten from the tungsten ore concentrates. However, the new emerging technologies, such as electrochemical reduction of the tungsten ore, (D. Tang et al., 2012; M. Erdoğan and I. Karakaya, 2010) should be appraised by considering both the economic aspect of the process and the properties of the tungsten powder that produced. For WC production, direct reduction of tungsten oxide or tungsten ore concentrate will be the trend for the future, since this will on one hand tailor the present cumbersome and costly two-step (tungsten powder production and carbonization) production process into a single one, and on the hand, this has the advantageous of producing WC powder with finer crystal structure of nanometer and with improved mechanical properties (P. Hoier, 2014). For the production of W-bearing steels, the direct use of tungsten ore should be appreciated, as the use of ferrotungsten can be avoided, which implies both fewer materials loss from the production chain and higher economy/energy efficiency.

## 26.3 TECHNICAL INNOVATIONS IN TUNGSTEN PRODUCTIONS FROM PRIMARY RESOURCES

### 26.3.1 MINERAL PROCESSING

Tungsten beneficiation plants normally operate with a recovery of 60-85%. The beneficiation recovery rate for the Mittersill tungsten mine in Austria has been estimated at 75–85%, whereas that for the Los Santos project in Spain has been reported at 57–65% and that for the Cantung mine in Canada is around 75–79% (Leal-Ayala et al., 2015). The main challenges in the operations of tungsten ore beneficiation which may affect process recovery and/or concentrate grade are as follows:

1) Scheelite ore has good floatability but it is often associated with other calcium containing minerals such as calcite, fluorite and apatite which have similar surface properties to scheelite. It is usually difficult to float scheelite from these minerals using conventional reagents (Yin and Wang, 2014).

2) In beneficiation process most of the losses of tungsten occur in slimes, which are difficult to be treated with conventional beneficiation techniques. The generations of tungsten mineral slimes are resulted from: the brittleness of the tungsten minerals, leading to their preferential grinding during the comminution stages; and due to the high density the tungsten minerals tend to go into over-size fraction or underflow during classification by hydrocyclones or hydraulic type of classifiers used in the grinding circuit, and get recycled to the grinding mill, leading to their over-grinding (Krishna, 1996).

3) The beneficiation flowsheet largely depends on the ore mineralization and the liberation size of tungsten minerals. Tungsten ores usually have complex mineralizations, i.e., complex mineral compositions and ore textures. Other metallic minerals are companied and the liberation of tungsten minerals can be found in a wide range of size from several mm to 10-20 µm. These factors cause beneficiation flowsheets complex.

4) Weathering and other alteration processes lead to secondary tungsten minerals such as hydrotungstite ($H_2WO_4 \cdot H_2O$), anthoinite ($AlWO_3(OH)_3$) and cerotungstite ($CeW_2O_6(OH)_3$). Presence of these minerals might cause lower process recovery and/or lower concentrate grade (Schmidt et al., 2012).

Generally, as the increase of exploitation the primary tungsten resources become poorer in grade, finer in grain size and more complex in mineralization which cause the mineral processing of the tungsten ores more difficult in the future (Xu et al., 2014).

The innovation studies in recent years on tungsten beneficiation are mainly concentrated on selective flotation of scheelite from other calcium containing minerals such as calcite and fluorite by using more selective reagents, very fine scheelite and wolframite flotation, optimization of complex tungsten ores concentration by using combinatorial gravity-magnetic-flotation process and recovery of associated Mo, Cu and Bi sulphides from tungsten ores.

## SELECTIVE FLOTATION OF SCHEELITE FROM CALCIUM CONTAINING MINERALS

Scheelite, as one of calcium containing minerals, has similar surface properties and floatability to other calcium containing gangue minerals such as calcite and fluorite which are commonly associated with scheelite in tungsten ores. With $Ca^{2+}$ species on their surfaces, the calcium containing minerals own the same reactive centre and have very similar surface reactivity to conventional fatty acid or sulphate/sulfonate collectors. The problem of flotation separation of them still remains unsolved without the addition of extra reagents (Deng et al., 2016).

After rough concentration of tungsten minerals the conventional Petrov's process is applied for further separation of scheelite from other calcium minerals which involves steaming of bulk concentrate in 2-4% solutions of sodium silicate ($Na_2SiO_3$) at 80-90°C using fatty acids as the collectors (Li and Li, 1983; Han et al., 2017). High energy cost occurs for this process because high temperature is required. In recent years, investigations have been carried out for improving the selectivity of scheelite from other calcium containing minerals by no heating processing.

There are two approaches of research on the reagent development in scheelite flotation. One is to develop more selective collectors for scheelite and another one is to develop effective depressants for the calcium containing gangues (Li et al., 2016).

**Studies on development of selective collectors for scheelite**

Currently, fatty acids such as oleic acid, linoleic acid, palmitic acid and sodium oleate, tall oil or oxidized paraffin soap are industrially applied in scheelite flotation (Bernhart, 2015; Han et al., 2017); Other types of surrfactants for scheelite flotation have been investigated either on theory using pure minerals or by testing using ores or minerals collected from tungsten mines. These collectors include anionic collectors other than fatty acids such as hydroxamic acids or hydroxamates (Han et al., 2017; Zhao et al., 2015; Qiu et al., 2001; Xia et al., 2004; Zhao et al., 2013; Deng et al., 2016; Pradip and Rai, 2003; Pradip et al., 2002; Gao, Y. et al., 2016; Zhang et al., 2016) and oleoyl sarcosine (Ozcan et al., 1994), cationic collectors such as quaternary ammonium salts and dodecylamine (Hu et al., 2011; Yang et al., 2015; Hiçyilmaz and Özbayoglu, 1992; Hiçyìlmaz et al., 1993; Gao et

al., 2015b; Wang et al., 2016), amphoteric collectors such as amino phosphoric acids (Hu and Xu, 2003), and mixed collectors, e.g. mixed cationic/anionic collectors (dodecylamine/sodium oleate) or mixed anionic/anionic collectors (sodium soap/ methyl ester sulfonate; octyl hydroxamic acid/ sodium oleate). However, most of these collectors are still in the theoretical study or laboratory test stage. The investigated collectors, methods and references are shown in Table 3.

Table 3 The investigated collectors, methods and references

| | Collector | Method | Reference |
|---|---|---|---|
| Hydroxamic acids or hydroxamates | Benzohydroxamic acid | Microflotation, Contact angle, FTIR spectra, XPS spectroscopy, Zeta potential etc., Industrial application | Han, H. et al. (2017); Zhao et al. (2015); Qiu et al. (2001); Xia et al. (2004) |
| | Naphthenic hydroxamates (cyclohexyl hydroxamic acid) | Microflotation, Zeta potential, Density Functional Theory (DFT) calculation | Zhao et al. (2013) |
| | Amide hydroxamates: N-(6-(hydroxyamino)-6-oxohexyl) benzamide N-(6-(hydroxyamino)-6-oxohexyl) octanamide N-(6-(hydroxyamino)-6-oxohexyl) decanamide N-(4-(hydroxyamino)-4-oxobutyl) octanamide | Microflotation, FTIR spectra, Zeta potential, XPS spectroscopy, Density Functional Theory (DFT) calculation | Deng et al. (2016) |
| | Alkyl hydroxamic acids (octyl hydroxamic acid) | Molecular modeling, Microflotation (Hallimond tube) | Pradip and Rai (2003); Pradip et al. (2002); |
| Cationic collector | Quaternary ammonium salts: didecyldimethylammonium chloride trioctylmethylammonium chloride dodecyltrimethylammonium chloride | Microflotation, FTIR spectroscopy, Zeta potential, Adsorption tests | Yang et al. (2015) |
| | Dodecylamine | Zeta potential, Microflotation, AFM observations, Contact angle measurements, MD simulations | Gao, Z. et al. (2015b) |

| | Amine D acetate | Flotation experiments, IR Spectroscopy | Hiçyilmaz and Özbayoglu (1992); Hiçyìlmaz et al. (1993) |
|---|---|---|---|
| | dodecylammonium chloride | Hallimond tube flotation experiments | Arnold et al. (1978) |
| Amphoteric collector | α-benzol amino benzyl phosphoric acid | Microflotation, Zeta potential, Adsorption measurement by UV spectrophotometer, IR Spectroscopy | Hu and Xu, (2003) |
| Collector mixture | Octyl hydroxamic acid / Sodium oleate | Microflotation, Zeta potential | Gao, Y. et al. (2016) |
| | Oleoyl sarcosine / Alkyl oxine | Flotation experiments, Nuclear Magnetic Resonance spectroscopy | Ozcan et al. (1994) |
| | Dodecylamine / Sodium oleate | Microflotation, Zeta potential | Wang, J. et al. (2016) |
| | Sodium soap ($C_{12-16}$ COONa) / Sodium fatty acid methyl ester sulfonate | Microflotation, Zeta potential | Gao, Z. et al. (2015a) |

It was reported that benzohydroxamic acid (BHA) has been used in the Shizhuyuan mine replacing fatty acid collector for scheelite flotation at room teperature since June 23, 2015 and the recovery was improved by almost 10% (Han et al., 2017). The dosage of BHA collector was 300– 400 g/t. Because of using BHA to replace fatty acid the dosage of water glass was decreased from 2–3 kg/t to 50–80 g/t but BHA needs to be mixed with lead nitrate ($Pb(NO_3)_2$) before adding in the conditioning vessel in the mole ratio of lead nitrate to BHA being almost 2:1. That is, the amount 1.2-1.6 kg/t of lead nitrate was added based on 300– 400 g/t of BHA. It was investigated that lead nitrate acts the activation of scheelite and wolframite with benzohydroxamic acid (BHA) as collector through binding of BHA and $Pb(OH)^+$ on the mineral surface (Zhao et al., 2015). Lead nitrate is a toxic and oxidizing agent. The impacts on environment of this process because of using a large amount of $Pb(NO_3)_2$ should be evaluated.

The resorption and reaction mechanisms of BHA on the surface of scheelite and other calcium containing minerals have been studied (Qiu et al., 2001; Xia et al., 2004). It was concluded that the –CONHOH groups in hydroxamic acids exhibit a strong chelating ability with metal ions exposed on the mineral surfaces through both O and N atoms.

Beside benzohydroxamic acid (BHA) other kinds of hydroxamates including naphthenic hydroxamates (cyclohexyl hydroxamic acid) (Zhao et al., 2013), amide hydroxamate (Deng et al., 2016), alkyl hydroxamic acids (octyl hydroxamic acid) (Pradip and Rai, 2003; Pradip et al., 2002; Gao et al., 2016) were also studied as the collectors for scheelite flotation.

The study by Zhao et al. (2013) indicated that cyclohexyl hydroxamic acid (CHA) has stronger collecting ability than BHA in scheelite flotation becasue the dianion of CHA exhibits higher atomic charge value, HOMO (Highest Occupied Molecular Orbital) energy, bigger dipole moment and binding energy with $Ca^{2+}$.

Deng et al. (2016) compared four amide-hydroxamic acid surfactants, N-(6-(hydroxyamino)-6-oxohexyl) benzamide (NHOB), N-(6-(hydroxyamino)-6-oxohexyl) octanamide (NHOO), N-(6-(hydroxyamino)-6-oxohexyl) decanamide (NHOD) and N-(4-(hydroxyamino)-4-oxobutyl) octanamide (NOBO), on scheelite and cilcite flotation based on flotation experiments and FTIR spectra, zeta potential and XPS analyses and concluded that at pH around 10, these four collectors displayed superior flotation performances to scheelite and weak collecting capacity to calcite (NHOD exhibited the best floatation performance of scheelite), and furhter they illustrated that the distances between O-O atoms (2.599, 2.852 and 2.796 A˚) for NHOD were matched well with the O–O distance in $WO_4$ (2.899 A˚ ) for scheelite compared to calcite.

For design and seleection of flotation reagents Pradip et al. (2002; 2003) compared the flotation of calcium containing minerals using octyl hydroxamic acid (HXMA-8) as the collector by molecular modeling method. Gao, Y. et al. (2016) studied octyl hydroxamic acid (HXMA-8) as an associate collector of sodium oleate (NaOl) in scheelite flotation. The flotation tests showed that mixed collectors of HXMA-8 and NaOl (total concentration $4.5 \times 10^{-4}$ mol/L, preferred mass ratio of 1:2) achieved the selective separation of scheelite from calcite at pH 8–10 and a lower dosage of sodium silicate (SS) (300 mg/L). Zeta potential measurements indicated that HXMA-8 adsorbed significantly on scheelite surface either in the absence or presence of SS by chemical bonding between oxygens of HXMA-8 and surface metal ions. NaOl also adsorbed on both mineral surfaces by chemisorption, but the adsorption on calcite surface was influenced adversely by the presence of SS. From this study it was concluded that using a hydroxamic acid as an associate collector of NaOl could decrease the dosage of water glass, but it was not indicated if there is a synergy of mixed two collectors on the selectivity of scheelite flotation.

Comparing to hydroxamic acids or hydroxamates the studies on the scheelite flotation using other kinds of anionic surfactants as collectors are much less. Early in 1994 the scheelite flotation was studied (Ozcan et al., 1994) from a low grade calcitic scheelite ore using oleoyl sarcosine as collector and alkyl oxine as modifier in laboratory and revealed that oxine and alkyl oxine have a modifying effect on scheelite flotation using oleoyl sarcosine as collector and increase both grade and recovery to a large extent by forming a complex compound on the scheelite surface. In addition, a collector combining sodium soap ($C_{12–16}$ COONa) with sodium fatty acid methyl ester sulfonate in the mass ratio of 4:1 demonstrated a high selectivity for the flotation of scheelite from calcite and fluorite (Gao, Z. et al., 2015a).

The isoelectric point of scheelite occurs at about pH 2, whereas those of calcite and fluorite occur at pH 8.2 and 9–10, respectively (Xu and Hu, 2003). So that, cationic flotation is considered an effective approach for separating scheelite from calcite at room temperature because of the significant difference between their surface charges.

Quaternary ammonium salts are usually halide salts with four alkyl groups attached to a central cationic nitrogen atom ($R_4N^+$). Flotation behaviors of scheelite and calcite with three quaternary ammonium salts, didecyldimethylammonium chloride (DDAC), trioctylmethylammonium chloride (TOAC) and dodecyltrimethylammonium chloride (DTAC)), were studied and compared with sodium oleate (Yang et al., 2015). Microflotation with single mineral and mixed minerals indicated that DDAC and TOAC were more powerful and selective collecors than oleate for scheelite flotation from calcite. Fourier-transform infrared spectra, and zeta potentials and dsorption isotherm analysis revealed that both electrostatic interactions and van der Waals forces play a primary role for adsorption of the quaternary ammonium salts on scheelite and calcite surfaces.

The different adsorption behavior of dodecylamine (DDA) on scheelite and calcite surfaces was mainly attributed to cationic $RNH_3^+$ species. The complex precipitates could also absorb through physical adsorption on each

mineral surface. But the DDA species were arranged more compactly on scheelite surface leading more hydrophobic (Gao et al., 2015b). Flotation behavior of scheelite and calcite was investigated using mixed cationic/anionic collectors of dodecylamine (DDA) and sodium oleate (NaOL) and compared with using individual NaOL or DDA by microflotation tests (Wang, J. et al., 2016). The flotation results of single mineral and mixed binary minerals demonstrated the mixed cationic/anionic collectors of DDA/NaOL at 2:1 molar ratio displayed a stronger collecting ability and higher selectivity for scheelite flotation than the individual collectors. The preferred order of collector addition was first DDA and then NaOL. The mixed DDA/NaOL collectors with addition of sodium silicate (SS) at pH 7 could achieve selective flotation of scheelite from calcite.

Flotation experiments carried out by Hiçyilmaz and Özbayoglu (1992) and Hiçyìlmaz et al. (1993) with real scheelite ore samples from a concentrator in Turkey showed that amine D acetate as collector gives the highest selectivity of scheelite from calcite comparing to other amines. Hallimond tube flotation experiments carried out on scheelite and calcite using dodecylammonium chloride as collector (Arnold et al., 1978) and shwed that the main variables were the calcium ion concentration and the pH. The addition of calcium chloride markedly lowered the recovery of scheelite but had no immediate effect on recovery of calcite. For good recovery of scheelite the pH should be above about 10 and excellent flotation of scheelite can be obtained event at about pH 7 by adding dodecanol together with dodecylammonium chloride.

Amphoteric collectors possess a cationic and an anionic function depending on the working pH. Over the recent years, amphoteric collectors, such as amino carboxylic and diphosphonic acids, have been found to show good selectivity in flotation separation of salt type minerals. A new amphoteric collector, α-benzol amino benzyl phosphoric acid (BABP), was synthesized and its collecting properties for calcium-containing minerals were examined through micro-flotation tests and the measurements of mineral electrokinetics and collector adsorption (Hu and Xu, 2003). The BABP exhibits selective collection for calcium-containing minerals, allowing preferential flotation separation by control of pulp pH. Using the BABP as a collector, fluorite can be floated over a pH range from 6 to 10, while calcite is floatable at pH between 8 and 10. Scheelite shows a limited floatability at pH around 8. The zeta potential measurement, collector adsorption determination and IR characterization revealed chemisorption as a main adsorption mechanism of amino phosphoric acids on the surfaces of calcium-containing minerals with monovalent collector anions being the active binding species and the extend of collector adsorption appears to be determined by surface calcium site density.

**Studies on development of effective depressants for the calcium containing gangues**

Sodium silicate ($Na_2SiO_3$) is conventionally used for depressing calcium containing gangues when fatty acids are used for scheelite flotation, but scheelite is also depressed to some extent. The depression mechanisms of organic and non-organic depressants of the calcium containing gangues were studied and the applications of these depressants were reviewed by Li et al., (2016). The addition of particular hydrophilic groups on the structures of depressants was suggested a useful method in the development of efficient depressants for the calcium containing gangues.

For $Na_2SiO_3$ the $SiO_2$ to $Na_2O$ ratio notably influences the depression of scheelite. Early in 1960-70s the role of both the alkaline and acidic water glass in scheelite flotation was investigated and showed that the latter had higher polymerizing ability, stronger hydrophilicity and very strong depressing effect on gangues (Li, Y. and Li, C. 1983). The effects of mixtures of sodium silicate and polyvalent cations ($Al^{3+}$, $Mg^{2+}$, $Cu^{2+}$, $Fe^{3+}$, $Zn^{2+}$, $Co^{2+}$, $Pb^{2+}$ and $Ca^{2+}$) on scheelite flotation were also studied. Babak and Viduetskii (1967) found that the addition of polycrylymide into the pulp can also improve the depression of $Na_2SiO_3$. The application of $Na_2SiO_3$ and CaO, the so-called "lime flotation process", gave rise to more satisfactory results.

Recently, a depressant called acidified sodium silicate combining sodium silicate with oxalic acid in the ratio of 3:1 was approved to be more selective than sodium silicate for calcite from scheelite with sodium oleate as a collector (Feng et al., 2015). The study showed that the pre-adsorption of acidified sodium silicate interferes with the adsorption of the collector (sodium oleate) on calcite surface while does not interfere with its adsorption on scheelite surface. In addition, a combination of sodium silicate with ferrous sulfate as the depressant for calcite and fluorite using an oxidized paraffinum sodium salt as a collector for scheelite was investigaed by using a scheelite ore from Yunan, China at the conditions of pH 10.5 and room temperature (Yang and Liu, 2015). A concentrate was achieved with grade 63.2% $WO_3$ and recovery 86.3%.

The study by Li, Y. and Li, C. (1983) suggested that the phosphates might be effective modifiers for selective flotation of scheelite from calcite and fluorite. Flotation tests indicated that sodium pyrophosphate and sodium hexametaphosphate are effective depressants for calcite and fluorite and weakly depressive for scheelite and the decreasing order of selectivity being as follows: $(NaPO_3)_6$ > $Na_4P_2O_7$ > $Na_3PO_4$.

Meng, X. et al. (2015) investigated the depression effects of $Na_2S$ on the gangue minerals in tungsten cleaning flotation and found that $Na_2S$ repels the adsorption of the collector on the surface of gangue minerals and reduces the activation function of metallic ions to them as well.

## FINE SCHEELITE AND WOLFRAMITE RECOVERY

In order to increase the recovery for low grade and finely disseminated mineral deposits many flotation operations need to improve the liberation of minerals by grinding them to very fine sizes (Miettinen, 2010). In the operations of tungsten concentration most of the losses of tungsten occur in slimes or very fine particles. Effects of fine particles (<10 μm)) on scheelite flotation were studied by testing and theoretical calculations (Yin and Wang, 2014). The low flotation rate and low recovery of hydrophobic fine particles are mainly due to their low efficiency of collision with bubbles (EC). Their EC values can be increased by either decreasing the bubble size or by aggregating the fine particles to an optimum size for flotation (Miettinen, 2010).

Carrier flotation is an effective method for increasing very fine minerals recovery. Carrier flotation of fine scheelite (-19 μm) was studied using polystyrene particles with the size of -100 μm+50 μm as the carrier of scheelite (Xiao and Chen, 2015). At the conditions of alkaline atmosphere and high agitation conditioning using sodium oleate as the collector the fine scheelite was effectively recovered. Single and multi layers of hydrophobic adsorption between the surface of polystyrene and scheelite particles were found by observation under an electronic microscope and the hydrophobic potential was calculated by EDLVO theory.

Cavitation is a process of in situ formation, growth and subsequent collapse of gas and/or vapor-filled cavities (microbubbles) in a fluid. Tiny bubbles generated by hydrodynamic cavitation were found to increase the contact angle of solids and hence attachment force, bridge fine particles to form aggregates, minimize slime coating, remove oxidation layers on particle surfaces, and in consequence reduce reagents consumption (Zhou et al., 2009). The aggregation behavior of ultra-fine scheelite particles induced by hydrodynamic cavitation was investigated (Zhou et al., 2016). The study confirmed that hydrodynamic cavitation can enhance the ultra-fine scheelite particles aggregation and their flotation, and nanobubbles generated by cavitation make the solid particles less negatively charged, thereby reducing the repulsive force between particles. At a low concentration of sodium oleate, particle aggregates could form in the slurry with treatment by hydrodynamic cavitation.

Wolframite is generally recovered by gravity methods as long as the particle size is sufficiently large. With a brittle feature wolframite is easily over-crushed and over-ground in the comminution circuits which causes the

formation of fine wolframite particles. The recovery of fine wolframite by gravity methods is normally below 45% (Ai et al., 2017a). Flotation of fine wolframite was investigated in recent years with sodium hydroxamate, octyl hydroxamic acid and benzohydroxamic acid as the collectors (Hu et al., 1997; Meng, Q. et al., 2015; Ai et al., 2017b). The tests (Meng, Q. et al., 2015) indicated that better floatability of wolframite was obtained at pH 7.0–10.0. The zeta-potential measurements and XPS analysis confirmed the chemisorption of these collectors on wolframite surface. The study on flotation of fine wolframite from the Shizhuyuan Mine in China using benzohydroxamic acid and fatty acid as the collectors revealed that the flotation kinetics of wolframite agree well with the modified first-order model (Ai et al., 2017b). Microflotation tests showed that the maximum recovery of fine wolframite (<38 µm) was achieved with the combination of sodium oleate, salicylaldoxime, benzohydroxamic acid and fatty-acid as the collector (Yang and Ai, 2016). The studies by Shang et al. (2015) and Yang et al. (2014) indicated that the floatability of wolframite is related to the iron-manganese ratio in wolframite which affects the reaction mechanism between the wolframite surface and the reagents.

## OPTIMIZATION OF BENEFICIATION FLOWSHEET OF COMPLEX TUNGSTEN ORES

The mixed wolframite-scheelite ores have the features of complex compositions, fine grain size and low head grade of tungsten. The processing of these ores were researched and advances in operations were made (Zuo and Gao, 2016). New flotation reagents and new beneficiation equipments were developed for processing these types of ores. The process of flotation combined with gravity and magnetic separations were commercially applied in tungsten concentrators. Applications of combinatory processes, combinatory flotation reagents and new types of flotation machines improved flotation efficiency of scheelite (Hao et al., 2016).

The beneficiation of a carbonate type wolframite-scheelite ore was investigated by mineralogical studies and beneficiation testwork (Chen et al., 2015). The process of high intensity magnetic separation followed by gravity separation using shaking tabling was tested for wolframite concentration, and the process of heated flotation followed by acid leaching was tested for scheelite concentration. A wolframite concentrate with grade 33.6% WO3 and a scheelite concentrate with grade 66.6% WO3 were obtained at the total recovery of 69.2%. At a wolframite-scheelite concentrator in China a beneficiation process was innovated (Mao et al., 2015) by adding high gradient magnetic separation (HGMS) to the stage of rough bulk wolframite-scheelite flotation to recover wolframite, and the rough wolframite and scheelite concentrates were cleaned separately by flotation in different streams. The wolframite cleaning tailings was returned to the rough flotation circuit while the scheelite cleaning tailings was processed using a suspension vibration cone concentrator to recover wolframite.

For a complex scheelite ore from a mine in Jianxi China with a low grade of tungsten and complex compositions of gangue minerals a combinatorial process of pre-flotation of sulphides followed by gravity concentration, room temperature rough flotation and heated cleaning flotation was designed and tested. Sodium carbonate (Na2CO3), water glass (Na2SiO3) and BK-418 were used as pH regulator, the depressant for gangues and the collector for scheelite, respectively. For the ore with the head grade of 0.18% WO3 a scheelite concentrate with grade 67.6% WO3 and recovery of 71.4% was obtained and the operational cost was decreased comparing to the previous process (Zhao, Y. et al., 2015).

For a complex and fine wolframite-scheelite ore a concentration process was developed (Gao, Y. et al., 2015) which contains the circuits of size classification, gravity concentration of coarse size fractions and slimes flotation. In the flotation circuit a combinatorial collector was used and in the gravity concentration circuit a centrifugal concentrator was used. For the ore with the head grade of 0.31% WO3 a coarse concentrate with the grade of 58.5% WO3 and a fine concentrate with the grade of 26.2% WO3 were obtained and the total recovery of tungsten was 77.0%.

## RECOVERY OF ASSOCIATED MO, CU AND BI SULPHIDES FROM TUNGSTEN ORES

Some valuable metals such as molybdenum (Mo), copper (Cu) and bismuth (Bi) are associated in the tungsten ores in the form of sulphides (Huang et al., 2016). The flotation of Cu and Bi sulphides and pyrite from a tungsten ore was investigated (Sheng et al., 2015; Zhong, 2015; Wang, Y., 2016; Wu and Zhou, 2015; Dai, 2016). These sulphides are normally floated prior to recovery of scheelite or wolframite using organosulfur compounds as the collectors dependent on sulphides such as butyl xanthate used for Mo flotation and diethyldithiocarbamate used for Bi flotation (Zhong, 2015). A process of bulk Cu-Bi-pyrite flotation and Cu/Bi/-pyrite separation at the grinding size of 76.3% passing 76 µm and the tailings as the tungsten concentrate was tested in a locked cycle flowsheet (Sheng et al., 2015). A copper concentrate with grade 21.4% Cu at recovery 94.8%, a bulk Bi-pyrite concentrate with grade 3.0% Bi at recovery 85.2% and a tungsten concentrate with grade 38.2% WO3 at recovery 89.3% were achieved.

For a scheelite ore containing Cu and Zn sulphides, pyrite and high pyrrhotite the process of pre flotation of Cu, magnetic separation of pyrrhotite, Zn flotation, pyrite flotation and re-concentration of tailings for scheelite recovery was tested (Wu and Zhou, 2015). For the ore with head grades 0.47% Cu, 0.91% Zn, 0.51% WO3 and 21% S a copper concentrate with grade 22.95% Cu at recovery 89.2%, a zinc concentrate with grade of 45.6% Zn at recovery 74.0%, and a scheelite concentrate grade 50.9% WO3 at recovery 79.0% were obtained.

The associated sulphides in the tungsten ores could have fine grain sizes and low liberation degrees. In a wolframite concentrator the recovery of the associated components (Cu, Mo and Zn) was improved by regrinding the middlings of shaking tables (Wang, Y., 2016). For a low grade scheelite-molybdenite ore (0.16% WO3 and 0.026% Mo) from a skarn scheelite deposit in Jiangxi China a testwork was performed using a process of bulk molybdenite-pyrite flotation, molybdenite/pyrite separation after regrinding, scheelite flotation at room temperature from the tailings (Dai, 2016). Effects of the parameters of grinding size, collector dosage, dosage of sodium carbonate, sodium silicate type and dosage were experimentally investigated. The locked cycle experiment at optimized conditions presented good grades and recoveries of concentrates, that is, a tungsten concentrate with grade 65.1% WO3 at recovery 85.4% and a molybdenum concentrate with grade 46.1% Mo at recovery 88.7% were achieved.

## 26.3.2 METALLURGICAL EXTRACTION

Due to the high dependence from Chinese exports, innovative concepts are necessary to guarantee a sustainable supply of tungsten, especially for resource-poor countries in the European Union. In the following, the future challenges for the hydrometallurgical recovery and processing of tungsten are described. Afterwards, some innovative concepts and studies are presented, which are not (yet) state-of-the-art processes, but have a high potential to be focused on for further research activities and industrial implementation (MSP-REFRAM D2.3, 2016).

## CHALLENGES

The leaching step is usually performed with a large excess of NaOH or NaCO3 at an elevated temperature and high pressure in steel autoclaves. In terms of resource efficiency, a future challenge is to save those reagents by reduction or substitution or to improve the operational conditions in order to increase the yield and produce lower amounts of waste streams. Additionally, the treatment in autoclaves consumes large amounts of energy.

The energy balance and a heat integration approach should be included in an overall economical and ecological evaluation (Personal communication with Wolfgang Kummer 2016).

The obtained sodium tungstate solutions are purified by precipitation in order to remove the main impurities like Si, Mo, As, Sb, Bi, Pb and Co. Here, the main focus lies again on the reduction of tungsten losses into the precipitation sludge. Maybe these sludges can internally be recycled or used for other low-grade products (Personal communication with Wolfgang Kummer 2016).

For the final conversion of tungsten into APT, solvent extraction or ion exchange resins methods are applied. A central question is, when and for which kind of feed stream is one of them preferred (Personal communication with Wolfgang Kummer 2016). Solvent extraction is performed from acidic media (pH 2-3), but the leachates are alkaline, which means, that large amounts of acid are necessary and large amounts of useless salts have to be removed from process.

On the other hand, the sodium tungstate solutions may be contacted with strongly alkaline ion exchange resins, where the tungstate is adsorbed. The central questions are, how can the treatment of the raffinate (digestion, waste reduction, energy saving) and stripping (stripping agent, ionic strength) be improved (Personal communication with Wolfgang Kummer 2016).

## INNOVATIVE PROCESSES

ACIDIC LEACHING WITH NITRIC AND PHOSPHORIC ACID

The state-of-the-art process for industrial scheelite leaching is the treatment with sodium hydroxide or sodium carbonate in an autoclaving process (Ullmann's Encyclopedia of Industrial Chemistry 2000; Zhao, 2011). However, these two leaching processes usually require high temperature and relatively large amounts of reagents to obtain high yields. This high excess of reagents causes a decrease of the leaching rate. The digestion had to be performed at high liquid/solid ratio, with a corresponding increase in heat consumption and decrease in the equipment capacity (Zhang et al., 2015). Additionally, the scheelite can be treated in an acidic leaching step with hydrochloric acid to produce tungstic acid (Ullmann's Encyclopedia of Industrial Chemistry 2000). This process has several disadvantages, as a solid-colloidal layer of tungstic acid covers the unreacted particles and hinders the reaction (Mo, 1984).

In a study of Zhang et al. (2015, 2016), scheelite was leached with a mixture of phosphoric in nitric acid (less corrosive to equipment than HCl) to produce a phosphotungstic acid solution, which is further treated by solvent extraction and the raffinate is recycled to the ore leaching stage. Here, the phosphoric acid acts as chelating agent and avoids tungstic acid precipitation. The acid consumption and waste water amount greatly decrease and the results show high recovery rates (Zhang et al., 2016). The proposed flowsheet is depicted in Figure 5. Because of the acidic leachate, there is no further acid needed prior the solvent extraction step.
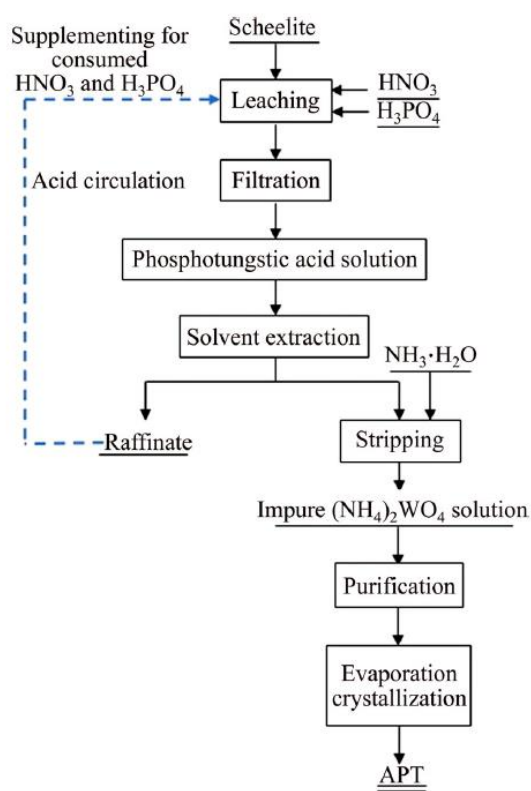
Figure 5 Flowsheet for APT production with acidic leaching with nitric and phosphoric acid [8].

BIOSORPTION

In a study of Ogi et al. (2016) tungsten is recovered selectively from tungsten-bearing scrap by biosorption. Traditional hydrometallurgical methods (solvent extraction, ion-exchange) usually consume high amounts of chemicals and energy and additionally generate toxic sludges and other waste products. Therefore, this study aims for the development of a more effective and environmentally friendly technology for the recovery of tungsten. Biosorption has been applied to several metals, for example Ag, Au, Cr, Cu, Fe, In, Ni, Pb, Pd, Pt, Rh, U, Re, Zn (Wang and Chen, 2009; Vegliò and Beolchini, 1997) using bacterial species. For tungsten biosorption, E. coli and beer yeast have high uptake capacities of 0.16 g tungsten/g biosorbent and 0.29 g tungsten/g biosorbent respectively, which is comparable to ion-exchange resins.

A flowsheet of recycling of used WC tip is shown in Figure 6. First, the WC scrap is calcinated at 950 °C for 12 h yielding $WO_3$ and $CoWO_4$ powder, which is treated with NaOH to obtain a $Na_2WO_4$ solution. At this stage, the biosorbent is added to the solution and the pH is adjusted to approximately 1, where W is adsorbed selectively and impurities like molybdenum and vanadium remain in solution. The W-adsorbed beer yeast is separated by centrifugation and dried at 80 °C for 12 h. After that, the beer yeast is burnt off in a furnace. Finally, the purified $WO_3$ powder is transformed into WC by reduction and calcination.

*1): RKF : Rotary Kiln Furnace
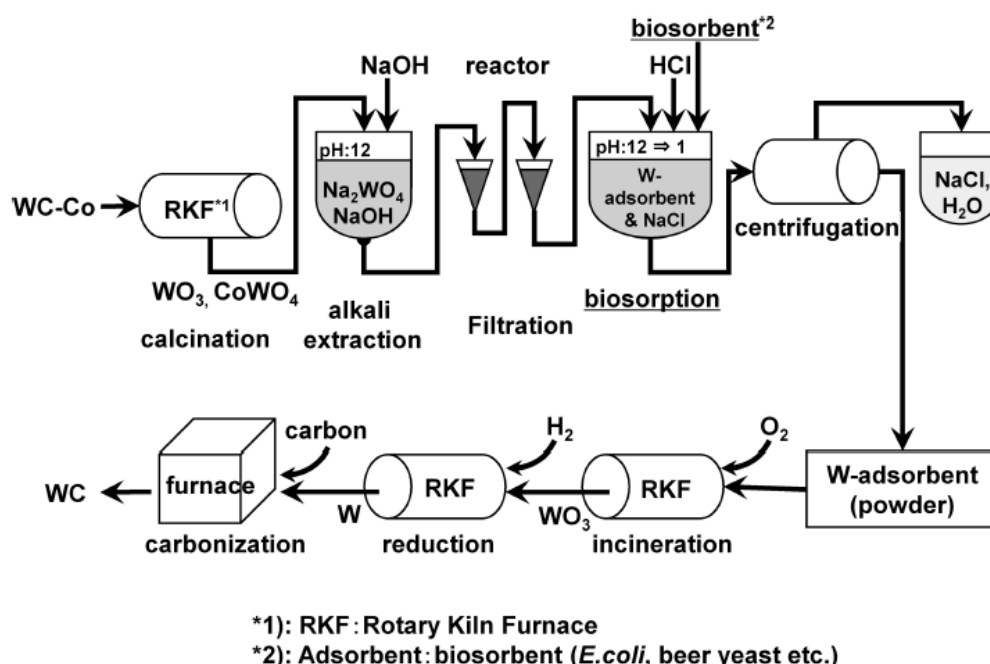*2): Adsorbent : biosorbent (*E.coli*, beer yeast etc.)

Figure 6 Flowsheet of tungsten recovery by biosorption (Ogi et al., 2016)

A feasibility study reveals, that this biosorption process is still more expensive than with the ion-exchange resin D301 (Table 4), but the required amount of chemicals are relatively small; large amounts quantities of acid and base substances are not necessary to remove tungsten from the adsorbent, which is a significant advantage.

Table 4 Comparison of cost performance of beer yeast and ion-exchange resin for 1 ton of recycled WC (Ogi et al., 2016).

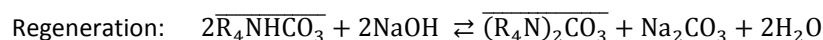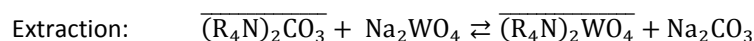| adsorbent | chemicals[a] | chemical amount needed (kg) | price of chemicals[b] (US$/kg) | price of chemicals needed for 1 ton of W recovery (US$) | sum of prices needed (US$) | displacement (L) |
|---|---|---|---|---|---|---|
| biosorption (beer yeast) | 15% HCl | 4880 | 0.20 | 488 | 1508 | 13388 |
| | beer yeast | 3400 | 0.30 | 1020 | | |
| ion-exchange resin (D301) | NH$_4$Cl | 735 | 0.17 | 124 | 489 | 71280 |
| | 25% NH$_4$OH | 400 | 0.39 | 156 | | |
| | 12% NaClO$_4$ | 192 | 0.90 | 173 | | |
| | NaOH | 24 | 0.01 | 0.24 | | |
| | D301 | 8573 | 1.00 | 36[c] | | |

[a]Chemicals required for ion-exchange resin are based on ref 23. [b]These values are for reference only. The prices of all materials were based on currently available prices from Alibaba.com (official site). [c]Ion-exchange change (D301), assumed to be recycled 240 times.

DIRECT SOLVENT EXTRACTION FROM ALKALINE MEDIUM

The traditional hydrometallurgical recovery of tungsten includes an alkali leaching, which is followed by a solvent extraction step (Lassner 1995; Paulino et al., 2012; Sato and Sato, 1995). This solvent extraction has to be conducted in acidic media (pH 2 - 3), as most of the industrial extractants (tertiary or secondary amines/quaternary ammonium salts) work in that range most efficiently. Thus, lots of acid is needed to neutralize and acidify the leach liquor and the valuable alkali (Na$_2$CO$_3$ or NaOH) and acid (H$_2$SO$_4$ or HCl) become useless inorganic salts. Additionally, anionic impurities of P, As, Si, Sn cannot be removed, because of the formation of

heteropoly acid. The precipitation of those impurities leads to a loss of tungsten (Luo et al., 2003). Therefore, the direct solvent extraction of tungsten from alkaline medium was proposed and studied (Drobnick and Lewis, 1964). The breakthrough was the application of quaternary ammonium carbonate salts as extractants, where the main reactions are expressed as (Zaitsev et al., 1992):

Extraction: $\overline{(R_4N)_2CO_3} + Na_2WO_4 \rightleftarrows \overline{(R_4N)_2WO_4} + Na_2CO_3$

Stripping: $\overline{(R_4N)_2WO_4} + 2NH_4HCO_3 \rightleftarrows 2\overline{R_4NHCO_3} + (NH_4)_2WO_4$

Regeneration: $2\overline{R_4NHCO_3} + 2NaOH \rightleftarrows \overline{(R_4N)_2CO_3} + Na_2CO_3 + 2H_2O$

Two major problems have restricted the industrial application for this process: poor phase separation and a relatively low tungsten concentration in the strip liquor (aprox. 100 g/l) resulting in high energy consumption in the following crystallization of APT by evaporation.

In a new study of Zhang et al. (2016), this direct solvent extraction from alkaline medium has been optimized to promote the application in commercial scale. Therefore, pilot (multi-stage mixer-settler system) and industrial (multi-stage annular centrifugal extractor) test plants were run over a longer period of time. Trioctyl methyl ammonium chloride was transformed into quaternary ammonium carbonate and used as extractant. The results of the pilot test with NaOH leaching liquor of wolframite concentrate are summarized in Table 5.

Table 5 Pilot test with NaOH leaching liquor of wolframite concentrate (Zhang et al., 2016)

| Item | $WO_3$ | Mo | P | As | $SiO_2$ | Sn | $Cl^-$ | $F^-$ |
|---|---|---|---|---|---|---|---|---|
| Feed (g/L) | 146.5 | 0.63 | 1.44 | 0.701 | 0.321 | 0.0018 | 3.09 | 2.62 |
| Strip liquor (g/L) | 152.5 | 0.92 | <0.005 | 0.009 | 0.034 | 0.0001 | 1.82 | 0.25 |
| Raffinate (g/L) | 2.14 | 0.041 | 1.20 | 0.623 | 0.480 | 0.0006 | 0.42 | 1.69 |
| Scrub raffinate (g/L) | 10.9 | 0.027 | / | / | / | / | 0.69 | 0.51 |
| Extraction (%) | 98.00 | 89.48 | / | / | / | / | / | / |
| Removal (%) | / | / | 99.67 | 98.77 | 93.60 | 94.66 | 43.40 | 90.83 |

The extraction rate reaches 98 %. Molybdenum is coextracted and needs to be removed in a consecutive precipitation step (Ullmann's Encyclopedia of Industrial Chemistry 2000). Other impurities like P, As, Si and Sn are almost removed quantitatively.

A flowsheet of the overall process is shown in Figure 7. The organic and the aqueous phase form closed cycles in the leaching-solvent extraction process, as well as $Na_2CO_3$ and NaOH. There is no consumption of acid and the precipitation of P, As and Si by precipitation is not necessary. Compared with the traditional technology, this technology shows the advantages of a shorter process, a high recovery rate, a low consumption of chemicals, and dramatically reducing the amount of waste water with obvious economic and environmental benefits producing a final product which meets the quality standards. It is reported, that the overall costs can be reduced by about US$ 400 per ton APT (Zhang et al., 2016).
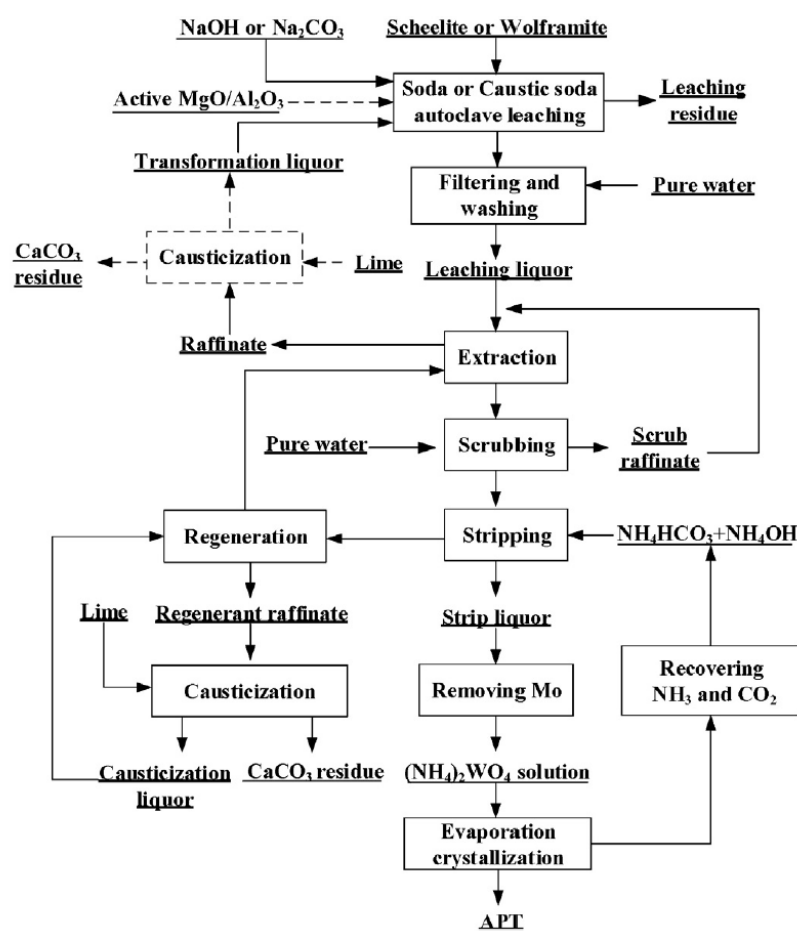
Figure 7 Flowsheet of tungsten hydrometallurgy based on direct solvent extraction from alkaline medium (Zhang et al., 2016)

EMULSION LIQUID MEMBRANES

Emulsion liquid membrane (ELM) techniques have been extensively investigated for the separation of metal ion, hydrocarbons and other biological compounds. ELM combines the two consecutive steps extraction and stripping within one single operation (Cussler et al., 1989). Therefore, the emulsion membrane phase (w/o emulsion) consists of a homogeneous mixture of extractant, organic diluent, an internal aqueous stripping phase and a surfactant for stabilizing the emulsion. The solute species from the external feed phase gets dissolve in the organic phase and diffuses into the internal strip phase. Finally, the enriched solute can be recovered by breaking of the emulsion (electro-coalescer, temperature etc.) (Noble and Stern, 1995). This transport of the solute through the liquid membrane is coupled with counter-transport of ions ($H^+$ or $OH^-$) from the internal stripping phase to the external feed phase ("facilitated transport"), which is the main driving force and allows high enrichment concentrations. On the other side, this driving force triggers an osmotic water flow and results in swelling or shrinking of the internal stripping phase and hence a loss of performance. Safety issues are another problem for an industrial realization. The first and only industrial ELM plant for zinc recovery in Austria burnt down due to a malfunction in the electro-coalescer (Bart, 1989).

Lende & Kulkarni (2015) investigated the ELM technique for the selective recovery of tungsten from a multi-component waste stream of printed circuit boards (Figure 8) in a stirred tank. Here, Aliquat 336 in hexane was used as organic phase and NaOH as internal strip phase. The two reaction mechanisms write as follows:

1. Extraction: $\quad WO_4^{2-} + 2\overline{(R_3CH_3N^+Cl^-)} \rightleftarrows \overline{(R_3CH_3N^+)_2WO_4^2} + 2Cl^-$
2. Stripping: $\quad \overline{(R_3CH_3N^+)_2WO_4^2} + 2Na^+ \rightleftarrows Na_2WO_4 + \overline{(R_3CH_3N^+)_2}$
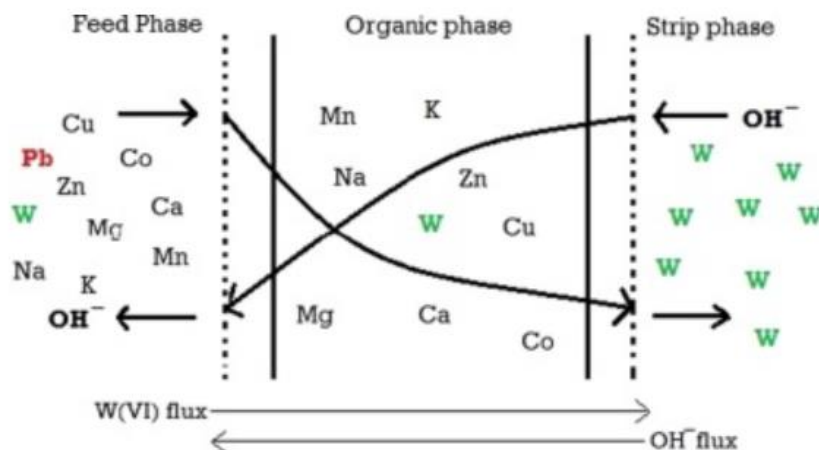


Figure 8 ELM process of selective tungsten recovery (Lende and Kulkarni, 2015)

In this study W(VI) (600 ppm) was selectively extracted from a multi-component feed, which mainly contains Pb (150 ppm) as co-elements. Under optimized conditions, the extraction efficiency was found to be 80 % with 4 times enrichment in the stripping phase. The separation factor for W(VI) vs. other co-ions was found to be very high thereby indicating selective recovery of W(VI) from the wastewater by using ELM process.

ELM is often conducted non-dispersively in hollow fiber modules (Fouad and Bart, 2008), where the emulsion is easier to split afterwards by a temperature shift, because of lower surfactant concentrations. The basic properties of ELM operations such as low-solvent inventory and high surface area make them ideal for the separation of solutes from dilute aqueous streams (Li, 1968).

MICROSTRUCTURED EXTRACTION PROCESSES

Recent developments in micro process engineering helped successfully to intensify existing solvent extraction processes of various metals (Willersinn and Bart, 2015; 2016). Here, a higher specific interfacial area and shorter diffusion distances lead to a higher number of theoretical stages. This is especially of interest for dilute feed streams for low-grade ores or tailings. Microextraction processes are either designed as slug-flow in a microchannel with alternating drops of aqueous and organic phase, non-dispersively in surface-modified microchannels or with an additional separating membrane between the two phases (Kenig et al., 2013). The advantage of a higher extraction efficiency is outweighed by a lower throughput compared to conventional extraction equipment. A higher throughput is achieved by numbering-up of many identical modules. Despite the superior extraction efficiency, the throughputs of big mixer-settler plants in extractive metallurgy cannot be realized.

## 26.4 CHARACTERIZATION OF MINING TAILINGS AND PROCESSING RESIDUES AND POTENTIAL UTILIZATIONS

### 26.4.1 MINING TAILINGS CONTAINING W

Mineral processing wastes are referred to in the Resource Conservation and Recovery Act (RCRA) as wastes that are generated during the extraction and beneficiation of ores and minerals. These wastes can be subdivided into a number of categories: waste rock, mill tailings, coal refuse, wash slimes, and spent oil shale (J.P. Castro-Gomes et al., 2012). Waste rock and mill tailings from mineral processing could be major secondary sources of metals including tungsten. Large amounts of waste rock are produced from surface mining operations, such as open-pit copper, phosphate, uranium, iron, and taconite mines. Small amounts are generated from underground mining.

Waste rock generally consists of coarse, crushed, or blocky material covering a range of sizes, from very large boulders or blocks to fine sand-size particles and dust. Waste rock is typically removed during mining operations along with overburden and often has little or no practical mineral value. Types of rock included are igneous (granite, rhyolite, quartz, etc.), metamorphic (taconite, schist, hornblende, etc.) and sedimentary (dolomite, limestone, sandstone, oil shale, etc.). It is estimated that approximately 0.9 billion metric tons (1 billion tons) of waste rock are generated each year in the United States (Liu, 2015).

Mill tailings consist predominantly of extremely fine particles that are rejected from the grinding, screening, or processing of the raw material. Typically, mill tailings range from sand to silt-clay in particle size, depending on the degree of processing needed to recover the ore. The basic mineral processing techniques involved in the milling or concentrating of ore are crushing, then separation by any one or more of the following methods including heavy media separation, gravity separation, froth flotation, or magnetic separation. About 450 million metric tons (500 million tons) per year of mill tailings are generated from copper, iron, taconite, lead, and zinc ore concentration processes and uranium refining, as well as other ores, such as barite, feldspar, gold, molybdenum, nickel, and silver (Liu, 2015)..

The global mass flows tungsten in 2010 was reported in the paper (Xiao, 2013). In 2010 the total 102.5 kt tungsten mass was contained in the mined ore from which 76.9 kt was produced in the tungsten concentrate. Total 30,300 $WO_3$ t was lost in the waste streams in which 25,600 t $WO_3$ was lost in the mine tailings and 4,700 $WO_3$ t in the processing residues. In 2010 $WO_3$ about 24% of the total tungsten production was from the End-of-life scrap. But the recovery of lost tungsten in the mine tailings and the processing residues has not been statistically reported.

Historical tungsten mine tailings, slimes in which tungsten minerals are difficult to be recovered such as in *Panasqueira mine in Portugal.* Currently, Panasqueira mining generates almost 100 tonnes of waste-rock per day. Mineral extraction and processing produce, primarily, two main types of mine tailings, accordingly to its grain size: coarse waste-rock tailings (sterile material) derived from rock blasting and waste-mud tailings (crushed and milled waste-rock) conveyed by pipelines into lagoons (mud dams), amounting to several million tons. In the 1980's Panasqueira mining was generating of about 300 tons of waste-rock tailings per day; currently, it is still generating almost 100 tons per day. In the tailings high content of arsenic in arsenopyrite was contained (Clemente et al.,1993).

In Luanchuan mine in China the tailings of the Mo flotation contain scheelite with grade 0.143% $WO_3$ (Ministry of industry and information technology of the people's Republic of China, 2010; Zheng et al., 2010) (Table 6)

Table 6 The chemical compositions of the Mo flotation tailings

|  | Mo | WO3 | S | P | As | Fe2O3 | SiO2 | Al2O3 | CaO |
|---|---|---|---|---|---|---|---|---|---|
| **Ore** | 0.224 | 0.148 | 1.87 | 0.24 | 0.059 | 6.97 | 43.64 | 3.95 | 27.06 |
| **Tailings** | 0.02 | 0.143 | 0.64 | 0.18 | 0.049 | 6.67 | 46.88 | 3.4 | 25.36 |
|  | **CaCO3** | **MgO** | **CaF2** | **Cu** | **Pb** | **Zn** | **Au (g/t)** | **Ag (g/t)** | |
| **Ore** | 6.73 | 1.77 | 4.76 | 0.038 | 0.035 | 0.046 | 0.96 | 20.33 | |
| **Tailings** | 5.24 | 1.46 | 5.02 | 0.02 | 0.024 | 0.031 | 0.56 | 6.03 | |

The particle size distribution and tungsten distributions in the size fractions are shown in Table 7.

Table 7 Particle size distribution and tungsten distributions in the size fractions

| Size fraction, mm | Weight, % | WO3 grade, % | WO3 distribution, % |
|---|---|---|---|
| +0.2 | 3.96 | 0.028 | 0.78 |
| -0.2+0.154 | 18.35 | 0.042 | 5.39 |
| -0.154+0.105 | 12.55 | 0.081 | 7.11 |
| -0.105+0.074 | 16.47 | 0.134 | 15.43 |
| -0.074+0.037 | 10.07 | 0.242 | 17.04 |
| -0.037+0.019 | 11.87 | 0.228 | 18.93 |
| -0.019+0.010 | 17.58 | 0.189 | 23.29 |
| -0.010 | 9.15 | 0.188 | 12.03 |
| Total | 100 | 0.143 | 100 |

The processing tungsten-bearing dumps and tailings produced from the Barruecopardo tungsten mine in Spain have the data (Ormonde Mining plc, 2006) in Table 8.

Table 8  Processing tungsten-bearing dumps and tailings produced from the Barruecopardo tungsten mine

| | Sample sites | Average WO3 % | | Average distribution | |
|---|---|---|---|---|---|
| | | -1 mm | +1 mm | -1 mm | +1 mm |
| Tailings | 13 | 0.093 | 0.088 | 73% | 27% |
| **Dumps** | 38 | 0.044 | 0.022 | 38% | 62% |

The material in the western part has higher tungsten grades of 0.1% WO3 and with a higher proportion of fine material amenable to direct spiral concentration.

The Bom-Gorhon tungsten ore deposits are located in the Petrovsky-Trans-Baikal area of Chita region in Russia. The Vein deposit contains tungsten mainly in the form of hubnerite (74-95%), the rest is scheelite. From the explored reserves 13.4 thousand tons have relatively high grade ($WO_3$ 0.917%). The enrichment of Bom-Gorkhon ore by a gravity method hundred thousand tons of the tailings with $WO_3$ content from 0.1 to 0.35% were accumulated. Besides the main element (tungsten), there are associated components – bismuth and tin (Frolova et al., 2014).
Tin tailings in Bolivia contains $WO_3$ (grade of 0.64%), and also Cu (grade of 0.84%) and Sn (grade of 0.84%), Tungsten is predominately present in wolframite and Tin in cassiterite (Xiao, 2013).

In order to effectively utilize industrial wastes, ceramic substrates was successfully prepared by conventional ceramic sintering process using tungsten mine tailings from different production regions in China as the main raw material (Liu et al., 2015)
Tailings from Cantung Mine was reported by North American Tungsten Corporation Ltd (2013).  All material from 1971-2007:  3.7 to 4.1 Mt (short tons), 0.29-0.35% $WO_3$, 0.24-0.28% Cu and 0.27-0.33 g/short ton.

The coarse tailings and slimes in La Parrila mine in Spain (La Parrilla Tailings, http://www.wresources.co.uk/projects/la-parrilla/la-parrilla-tailings/). In the period 1968-1986 the 7 Mt of ore processed produced some 2 $Mm^3$ of coarse tailings and 1.2 $Mm^3$ of slimes. In 1980-1982 a 1,000kg composite sample were collected from various places from the tailings pond and returned a grade of 0.28% $WO_3$.

In Kolar and Hutti gold fields in India (Rao and Subrahmanyan, 1986) scheelite is associated with gold mineralization. The old tailing dumps of Kolar were worked for recovery of tungsten (in 1986) (Walker dump

and Balaghat dump). Scheelite content from 0.01% to 0.53% WO3. Scheelite from old dumps: the Walker dumps amounting to 17 tons at 0.18% WO3, and Balaghat dumps with 81 tons at 0.04% WO3 are processed for recovery of scheelite.

## 26.4.2 METALS COMPREHENSIVE RECOVERIES AND UTILIZATIONS OF W CONTAINING TAILINGS

Tungsten mine tailings usually not only contain tungsten but also include other valuable metals such as Cu, Mo and Bi and non-metal minerals which could be comprehensively recovered or utilized (Lan et al., 2016).

Comprehensive recoveries of Cu, W and Sn were achieved from a tin tailings containing tungsten (0.64% WO3) and also Cu and Sn in Bolivia. The combined different techniques chlorination, flotation, high intensity magnetic and gravity separations are applied in the process (Xiao et al., 2013). After the chlorination segregation flotation, high intensity magnetic separation, gravity separation, were applied and the technological parameters are optimized as follows: the segregation temperature 950 ℃, segregation time 45 min, calcium chloride dosage 3%, coke dosage 3%, primary grinding fineness P95 ＜74 μm, magnetic field intensity of high intensity magnetic separation H=1.0 Tesla, and secondary grinding fineness P95＜38 μm. Under the optimal conditions, the copper concentrate with Cu grade of 25.04% at recovery of 83.19%, tungsten concentrate with WO3 grade of 60.22% at recovery of 64.26%, tin concentrate with Sn grade of 40.11% at recovery of 65.59% were obtained, respectively.

Mining and quarrying activities in Europe generate approximately 55% of total industrial wastes, according to a recent Eurostat report. Most of these wastes are directly dumped on land or deposited in landfill sites (J.P. Castro-Gomes et al., 2012). The potential for reuse of waste-rock piles of Panasqueira tungsten mine was discussed (J.P. Castro-Gomes et al., 2012). Such materials must have suitable properties for technical-artistic value added applications, such as conservation, restoration and/or rehabilitation of historic monuments, sculptures, decorative and architectural intervention, or simply as materials for building revetments.

Using tungsten mine tailings as the main raw material ceramic substrates successfully was prepared by conventional ceramic sintering process (Liu et al., 2015). Material properties including density, porosity, corrosion resistance performance, mechanical strength were measured and showed the ceramic substrate from tungsten mine tailings could be potential in applications.

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# 27 VANADIUM

## 27.1 PRODUCTION LINES OF IDENTIFICATION FROM PRIMARY RESOURCES

### 27.1.1 GLOBAL PRODUCTION

Vanadium are known mainly present in deposits of phosphate rock, titaniferous magnetite, bauxite as well as in deposits of fossil fuels such as oil and coal. [1], [2] Although the world resources of vanadium exceed 63 million tons, some deposits are not available for the vanadium production.[1] Titaniferous magnetite ore is identified as the most important resources of vanadium and the ore concentrate usually contains 1.0% to 1.5% $V_2O_5$.[3] By far, 85% of vanadium production is from the titaniferous magnetite (26% from the primary titaniferous magnetite mines and 59% from vanadium slag generated from the processing of titaniferous magnetite ore in steel production) and 15% from the other resources (such as catalyst and residuals from the power plant fired with heavy oils). [2][3][4][5] According to U.S. Geological Survey the global vanadium supply from the mine in 2015 amounted to 79400 tons and was dominated by China (53%), South Africa (24%), Russia (19%) and Brazil (3%), as shown in Figure 28.[1] The major vanadium producers are listed in **Table 10**.
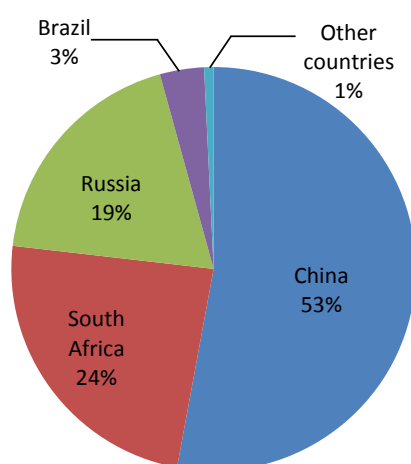


**Figure 28** Global mine production of vanadium by shares in different countries in 2015 (in total around 79400 tons).[1]

**Table 10** Major Vanadium producers.[6]

| Country | Company |
|---|---|
| China | Hebei Iron & Steel Group |
| | Pangang Group Vanadium Titanium & Resources |
| Russia | EVRAZ Vanady Tula |
| U.S. A. | EVRAZ Stratcor |
| South Africa | Glencore Rhovan |
| Austria | Treibacher |
| Czech Republic | EVRAZ Nikom |
| Brazil | Largo Resources |

## 27.1.2 APPLICATIONS

Around 80% of vanadium (in the form of oxide) is used to produce ferrovanadium, which is further used to alloy steels with vanadium, especially HSLA steels and special steels. Vanadium oxide is also used as catalyst and as pigment for ceramics and glass.[2], [4] The global end-use of vanadium is shown in **Figure 29**.

As shown in **Figure 29**, 60% of vanadium is used to produce HSLA steels. The vanadium contents in the HSLA steels vary with the types of steels, but normally the vanadium content is in the range of 0.01-0.15%.[8], [9] Considering both the amount of vanadium used in the HSLA steels and their vanadium content, the production volume of HSLA steels is huge. Vanadium in special steels (such as high-speed tool steels) accounts for the second largest consumption of vanadium with a share being 30%. Vanadium contents in the special steels are normally higher, ranging from 0.1-5%.[10] Vanadium improves the strength of titanium alloys and promotes their thermal stability. Several important commercial titanium alloys contain 2.5-15% vanadium.[10]
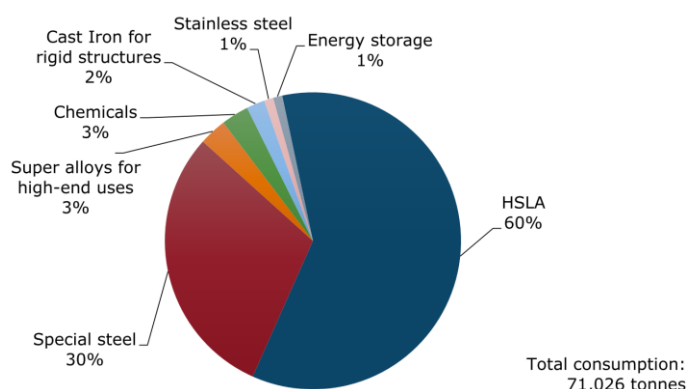


**Figure 29** Global end-uses of vanadium (average figures for 2010-2014). [2]

## 27.2 PROCESSING TECHNIQUES RECOGNITION AND ANALYSIS

## 27.2.1 MINERAL PROCESSING

As mentioned earlier, titaniferous magnetite is the main mineral used for vanadium production. To obtain titaniferous magnetite concentrate, the Run-of-mine ore is crushed, ground screened and magnetically separated to remove the gangue materials.[6] A flowsheet for the mineral processing of titaniferous magnetite at Mapochs Mine in South Africa is shown in **Figure 30**.
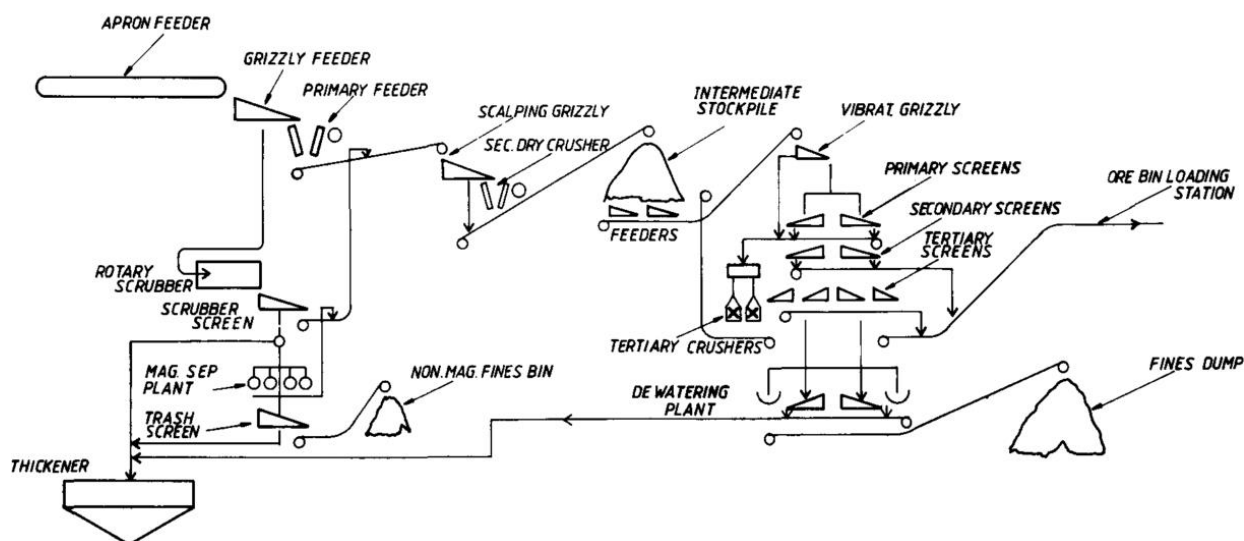
**Figure 30** Flowsheet for the mineral processing of titaniferous magnetite at Mapochs Mine in South Africa.[11]

## 27.2.2 METALLURGICAL PROCESSING

The Metallurgical processing of vanadium mainly involves three steps:

i) Vanadium oxide ($V_2O_3$ or $V_2O_5$) production. Vanadium oxide can be directly produced from titaniferous magnetite concentrate by the roast-leach process. It can also be indirectly produced from titaniferous magnetite concentrate by a series of steps to obtain vanadium oxides: (a) the reduction and smelting of titaniferous magnetite concentrate to obtain V-rich hot metal (FeV melt); (b) oxidization of the V-rich hot metal to obtain the V slag (also called V spinel slag or vanadiferous slag) and (c) applying the similar roast-leach process to obtain vanadium oxide. The two process routines for vanadium oxides production is shown in **Figure 31**.

ii) Ferrovanadium (FeV) production. Ferrovanadium production can either be produced by using vanadium oxide to produce FeV80 or be produced by using the FeV slag to produce FeV40-50. Lower grade FeV40-60 is often produced from secondary materials such as catalyst.

iii) V-containing steel production. V-containing steels are normally produced by adding ferrovanadium into the ladle or EAF to alloy steels with vanadium.
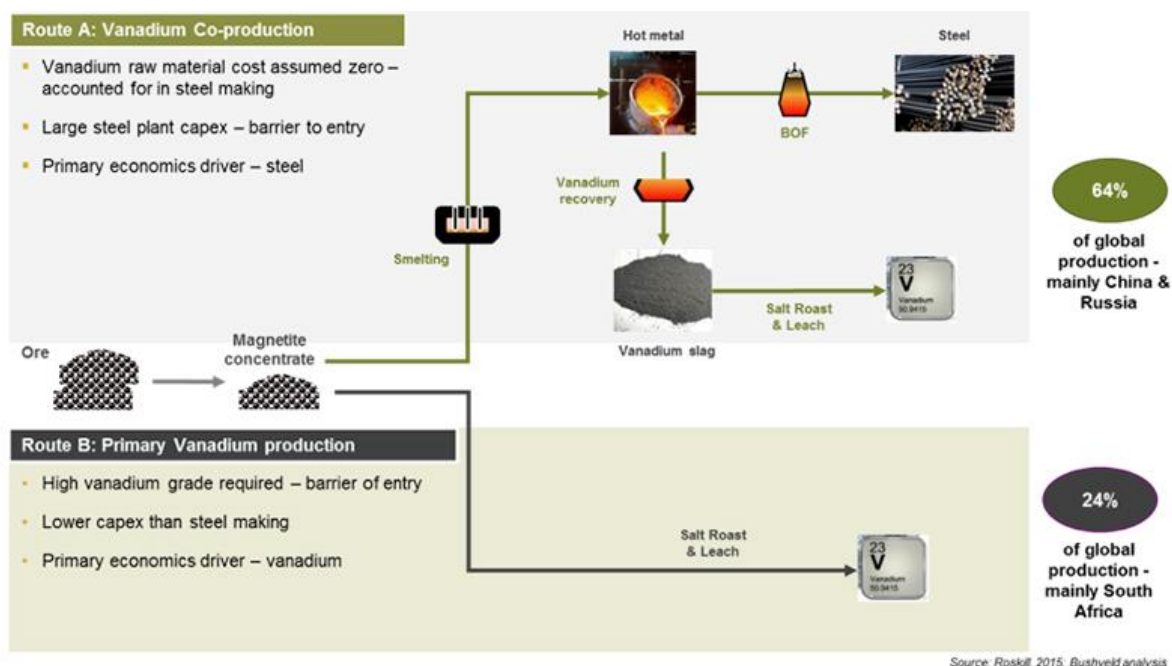
Route A: Vanadium Co-production
- Vanadium raw material cost assumed zero – accounted for in steel making
- Large steel plant capex – barrier to entry
- Primary economics driver – steel

Route B: Primary Vanadium production
- High vanadium grade required – barrier of entry
- Lower capex than steel making
- Primary economics driver – vanadium

Source: Roskill, 2015; Bushveld analysis

**Figure 31** Two process routines for Vanadium oxide production from the titaniferous magnetite concentrate. [12]

## 27.2.2.1      VANADIUM OXIDE PRODUCITON

**2.2.1.1 Vanadium oxide production directly from titaniferous magnetite concentrate**

Vanadium oxide can be produced directly from titaniferous magnetite concentrate by applying the roast-leach process.[6], [13], [14] The roast-leach process typically consists of four stages, namely, roasting, leaching, precipitation and calcination. In the roasting stage the concentrate is blended with $Na_2CO_3/NaCl/Na_2SO_4$ and subjected to high-temperature (e.g. 900-1200 °C for $Na_2CO_3$) treatment, during which vanadium in the concentrate is converted to soluble sodium vanadate (NaVO3). The use of $NaCl/Na_2SO_4$ during the roasting can cause the formation of corrosive gases such as $Cl_2$, HCl and/or $SO_2/SO_3$, therefore $Na_2CO_3$ is normally used. In the leaching stage the roasting product is leached with water and sodium vanadate solution is obtained. Further, vanadium is recovered from the pregnant leach liquor by precipitation with an excess of ammonium chloride or sulphate solution to either ammonium (poly)vanadate (APV) or ammonium metavanadate $NH_4VO_3$ (AMV). The precipitate is typically calcined to remove crystalline water and ammonia and produce a high-purity $V_2O_5$ material ($V_2O_5 > 99.5\%$ ). [12] A flowsheet of the roast-leach process is shown in **Figure 32**.
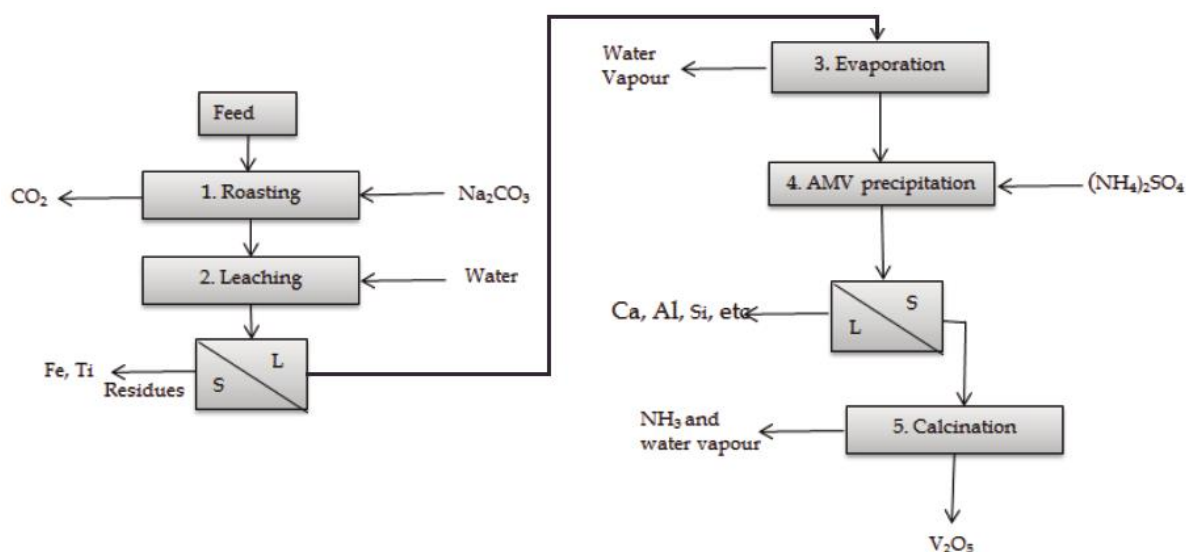
**Figure 32** Roast-leach processing flowsheet of vanadium oxide production from titaniferous magnetite concentrate.[14]

Compared to the reduction-smelting process for vanadium oxide production, the roast-leach process directly from the concentrate has the advantage of high cumulative vanadium recovery.[13] The yield of vanadium from the roast-leach process is around 82% [13], [14] and the loss of the vanadium is due to the incomplete transformation of vanadium to sodium vanadate. This direct roast-leach process is exemplified by Glencore Xstrata in South Africa and Australia.[6] The big drawback is the large amount of solid waste that is generated, which is the about same quantity as the feed into the treatment.

**2.2.1.2 Vanadium oxide production indirectly from titaniferous magnetite concentrate**

   (a)   Production of V-rich hot metal by reduction and smelting of titaniferous magnetite concentrate

The reduction and smelting of titaniferous magnetite has two different processes. The first one is the blast furnace (BF) ironmaking process. In this process the titaniferous magnetite (in the form pellets or sinter), is charged into the BF, where the iron and vanadium in the titaniferous magnetite is reduced. The product from this process is V-rich hot metal, which contains 0.3-0.5% vanadium. The main issue regarding reduction and smelting of titaniferous magnetite in the BF lies in the formation of carbonitride (TiN and TiC), which increases the viscosity and refractoriness of the slags and thus adversely affects the BF process.[15] To overcome this issue the BF is typically operated with high slag ratio at the expense of low energy efficiency.[4] However, when the contents of titanium oxides in the titaniferous magnetite exceeds certain limit, it may not be possible at all to smelt the titaniferous magnetite in the BF.[16] At the moment this process is applied widely as for example in China and Russia.[4], [12] The second process for reduction and smelting of titaniferous magnetite is the submerged-arc furnace (SAF) process, which is characterized by the pre-reduction of the titaniferous magnetite in the rotary kiln followed by the smelting of the DRI in the SAF.[17] At present this process is applied at New Zealand Steel (The process was also applied in the former Highveld plant), which produces a hot metal (FeV melt) containing 0.4-0.5 vanadium.[4], [17]

   (b)   Production of the vanadium slag from the V-rich melt

In principal the vanadium slag is produced by oxygen blowing in combination with solid oxidants and coolants (such as mill scale, iron pellets and iron scrap) into the V-rich melt (containing 0.3-0.5% vanadium), during which

the vanadium in the melt is oxidized and ended up in the slag. The working temperature of the processes is at or below 1400 °C to achieve low rate of decarburization. At present there are two different processes applied in the industry for production of vanadium from the V-rich hot metal. The first one is the ladle treatment process. In this process the hot metal is subjected to oxidation in the transfer ladle to produce vanadium slag. New Zealand Steel is the only plant in the world that carries out V extraction from hot metal in the ladle. Another process for the production of vanadium slag from the hot metal is the duplex process. In this process the V-rich hot metal is firstly subjected to oxidation in the BOF converter without addition of lime to produce the vanadium slag and a carbon-bearing product (around 3% carbon), the latter is converted to steel in a second converter with the addition of necessary slag-forming materials to remove the impurities.[4]

The vanadium slag is commonly produced without additives, since high contents of CaO and MgO in the slag would have a large negative impact on the downstream roast-leach process. These slags typically contain 9-15% vanadium, up to 6% $Al_2O_3$, up to 5% CaO, 5-8% MnO, 10-17% $SiO_2$ and some amount of MgO, the latter of which is partially from the furnace lining. The residual vanadium in the hot metal is normally lower than 0.06%.[4]

The vanadium slag is normally crushed to recover the lumps of iron by magnet. Thereafter, the slag is ground to about 4mm and prepared for the downstream extraction process.

(c) Extraction of vanadium oxides (V2O5 or V2O3) from the vanadium slag

The extraction of vanadium oxides (V2O5 or V2O3) from the vanadium slag is also carried out by applying the roast-leach process as described earlier. Soda roasting is however normally carried out at a lower temperature of maximum 800-850°C to avoid extensive melting and damage of the roaster.The cumulative yield of vanadium from the titaniferous magnetite concentrate has been reported to be 71% in the FeV slag and 58% in the final vanadium oxide. [14]

## 27.2.2.2     FERROVANADIUM PRODUCTION

(a) Ferrovanadium production from vanadium oxide[4], [18]

Vanadium oxide can be reduced by carbon, silicon and aluminum to produce ferrovanadium. Carbothermic reduction of vanadium oxide is endothermic and therefore the process requires a lot of energy. The charge mainly consists of vanadium oxide, carbon source (coke, coal, etc.), steel scrap and fluxing agents. A typical ferrovanadium composition for this process is as follows: 33-42 % V, 3-5 % Si, 3-3.5%C and balance Fe. The high residual carbon content in the alloy and the difficulty in regulating the carbon content have made carbothermic reduction in the arc furnace less attractive than alternative routes. Silicothermic reduction of vanadium oxide takes place via two stages. In the first stage vanadium pentoxide is smelted to produce ferrovanadium containing about 30% vanadium with a considerable amount of residual silicon. The primary metal is refined with vanadium pentoxide and lime in a second stage and the secondary slag is returned as part of the charge to produce primary metal in the first stage. Lower vanadium oxides such as $V_2O_3$ and VO interact with silica to form vanadium silicates, thus making the reduction process difficult and more complicated. As a result the slag traps some vanadium and the recovery of vanadium rarely exceeds 75-80% .

At moment, aluminum is most widely used as the reducing agent. The reduction of vanadium oxide by aluminum can be subdivided into aluminothermic process and the electro-aluminothermic process. With respect to the aluminothermic process, the charge mix consists mainly of $V_2O_5$, scrap iron, aluminium (particle size: 0.7 - 1.1mm) and lime. The reaction between $V_2O_5$ and Al is strongly exothermic and once it has been initiated it can both melt the iron added to make the alloy and allow for effective separation of the alloy and the slag. With respect to the electro-aluminothermic process, the charge mix consists of either V2O5 and/or $V_2O_3$, scrap iron, aluminum and

lime. Without electrical heating, processing of solely $V_2O_3$ is not possible. The electro-aluminothermic process is normally carried out in the arc furnace, as shown in **Figure 33**. The produced ferrovanadium by the aluminothermic reduction contains around 75-85% vanadium and the yield of vanadium is around 95%. The aluminum consumption is 40% lower if the FeV is processed from V2O3 compared to V2O5.
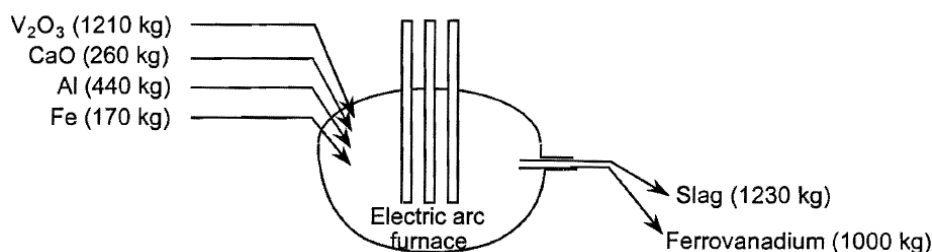
**Figure 33** FeV80 production from V2O3 in the electric arc furnace.

(b) Ferrovanadium (FeV) production from vanadium slag[4]

A large cost component for production of FeV80 is the roast-leach process for the production of the V2O3/V2O5 feedstock. A direct route to produce ferrovanadium only concerns pyro-metallurgical processing of the vanadiferous slag itself and therefore implies considerable cost savings. As the V/Fe ratio in vanadiferous slag rarely exceeds 0.5, a 1-stage process, as the electroaluminothermic method, would result in an alloy with maximum 20-30% V. For that reason, two- and three-state processes have been proposed in order to prepare alloys with normally 40-50% V.

In the two-state process, the iron oxide in the vanadiferous slag is reduced substantial in the first stage to produce a "de-ironed" (de-Fe) slag. The de-Fe slag is then subjected to further reduction by using stronger reducing agents in the second stage to produce ferrovanadium. In the 3-stage process, the V-slag is first reduced with carbon into a vanadium silicide having 25-60% Si. De-Fe slag can then be used to refine the vanadium silicide to lower its Si content to 10-20% and add V to the final alloy. The de-Fe slag is produced in a separate stage where vanadium silicide is used as reductant; the Si equivalent must be kept low in order for the V in the silicide to report to the de-Fe slag. The produced ferrovanadium directly from the vanadiferous slag contains 40-50% vanadium.

### 27.2.2.3    V-CONTAINING STEEL PRODUCTION

V-containing steels are usually produced by adding ferrovanadium into the ladle, during which the iron melt is alloyed with vanadium. Since the vanadium has high affinity to oxygen, the ferrovanadium is usually added in the semi-killed steels, fully killed steels and even vacuum-degassed steels. Recoveries of vanadium during the alloying will be at least 85% in semi-killed grades and as high as 95% in fully killed steels, especially when vacuum degassed. V-containing steels are also occasionally produced by directly adding ferrovanadium into the EAF just before tapping. In such case, double slag practice must be followed, rabbling the vanadium through the slag if necessary. Additions can be in the form of carbide/nitride or technical oxide under suitable reducing conditions. Final chemistry adjustments are always made in the ladle. Adequate superheat must be considered if major vanadium additions are made in the ladle, because vanadium addition agents are endothermic.[9]

### 27.3 VALUE CHAIN, IDENTIFICATION OF SECONDARY RESOURCES AND LOSS OF VANADIUM INTO THE ENVIRONMENT

According to the primary flow of the vanadium, the primary value chain of the vanadium can be drawn, as shown in **Figure 34**, in which the secondary resources of vanadium can be identified as follows and the potential loss of vanadium into the environment can be seen as well.



**Figure 34** Value chain of vanadium.

(i)     Tailings. The tailings are generated during the mineral processing of the primary ore, especially from titaniferous magnetite ore. Some of these tailings can be reprocessed to extract the vanadium.

(ii)    Roast-leach residuals. As described earlier, the vanadium in the primary ore and slag are mainly processed by the roast-leach process to produce vanadium oxide. During this process, the vanadium recovery is around 82% while the other vanadium is mainly lost in the roast-leach residuals (in the solid waste). These residuals can be regarded as an important secondary resource of vanadium.

(iii)     Slag generated during the various smelting processes. Slag generated during the smelting processing also contains a significant amount of vanadium and should be regarded as secondary resource.

(iv)     End-of-life products. According to the primary use of vanadium in the end products, steel scrap/alloys and spent catalysts are regarded as important secondary resources.

(v)      Miscellaneous residuals. Some residual materials, such as fly ash from heavy-oil fired power station also contain vanadium; they can also be taken as secondary resources.

The loss of vanadium to the environment (sometimes may also refer to loss to the other products) is mainly due to the non-fully recovery of vanadium in various processes, the dilution of the vanadium to other products (such as other steels), the discard of the End-of-life products, etc.

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