Monazite

Bastnasite

SEPARATION SCIENCE AND TECHNOLOGY EDUCATION: EXTRACTIVE METALLURGY PERSPECTIVE

Dr. Corby G. Anderson
Harrison Western Professor

The Kroll Institute for Extractive Metallurgy
Colorado School of Mines

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METALLURGICAL & MATERIALS ENGINEERING

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Colorado School of Mines

- *Est. 1874*
- *Golden, Colorado*
- *21 majors*
- *193 Faculty*
- *4300 students*
- *"…have a unique mission in energy, mineral, and materials science and engineering…"*
- *"has the most stringent admission standards of any US public engineering school."*
- *"Average starting salary of a BSc Mines graduate is $ 10 K more than an Ivy League graduate."*

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The Kroll Institute for Extractive Metallurgy

Dr. Patrick R. Taylor, Director KIEM

George S. Ansell Department of Metallurgical & Materials Engineering, Colorado School of Mines

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"KIEM - Excellence in Education and Research for the Mining, Minerals and Metals Industries"

- <u>History</u>: *The Kroll Institute for Extractive Metallurgy was established at the Colorado School of Mines in 1974 using a bequest from William J. Kroll.*
- *This effort was led by Professor Al Schlechten. 40 years, the Kroll Institute has provided support for a significant number of undergraduate and graduate students who have gone on to make important contributions to the mining, minerals and metals industries.*

The presentation of the first William J. Kroll Zirconium Medal to Admiral H. G. Rickover by Professor A. W. Schlechten, Director of the Kroll Institute for Extractive Metallurgy in 1975.

- ***<u>Objectives</u>: The objectives of KIEM are to provide research expertise, well-trained engineers to industry, and research and educational opportunities to students, in the areas of : minerals processing, extractive metallurgy, recycling, and waste minimization.***

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KIEM - Kroll Institute for Extractive Metallurgy &
CR [3] - Center for Resource Recovery & Recycling

Patrick R. Taylor

Director, KIEM
G.S. Ansell Distinguished Professor of Chemical Metallurgy

EXPERTISE

- **Mineral Processing**
- **Extractive Metallurgy**
- **Recycling**
- **Waste Treatment & Minimization**
- **Thermal Plasma Processing of Materials**
- **Thermal Plasma Processing of Wastes**

Gerard P. Martins

Professor of Metallurgical and Materials Engineering

EXPERTISE

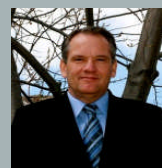
- **Process and extraction metallurgy**
- **Engineered ceramic and metal powders**
- **Electrochemical systems**
- **Corrosion**
- **Transport phenomena**
- **Reactor Design**

Brajendra Mishra

Director, CR[3]
Associate Director KIEM,
Professor of Metallurgical and Materials Engineering

EXPERTISE

- **Pyrometallurgy**
- **Electrochemistry**
- **Materials synthesis**
- **Waste Processing**
- **Recycling**
- **Molten Salt Processing**
- **Oxidation**



Corby G. Anderson

Harrison Western Professor of Metallurgical and Materials Engineering

EXPERTISE

- **Extractive Metallurgy**
- **Engineering Design**
- **Transport Phenomena**
- **Economics**
- **Reactor Design**
- **Kinetics**
- **Mineral Processing**
- **Recycling**
- **Waste Treatment & Minimization**

D. Erik Spiller

Research Professor of Metallurgical and Materials Engineering

EXPERTISE

- **Mineral Processing**
- **Comminution**
- **Physical separation**
- **KineticsFlotation**
- **Leaching**
- **Liquid-solid separation**
- **Project management**

Paul B. Queneau

Research Professor of Metallurgical and Materials Engineering

EXPERTISE

- **Extractive and process metallurgy**
- **Pyrometallurgy**
- **Recycling**
- **Waste treatment and minimization**

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CRITICAL ASPECT OF CRITICAL MATERIALS

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CRITICAL MATERIALS

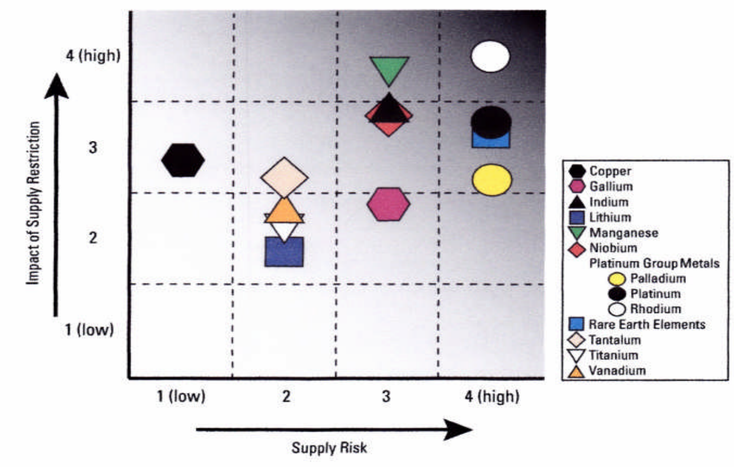

Figure 3. Criticality matrix for selected imported metals (National Research Council, 2008).

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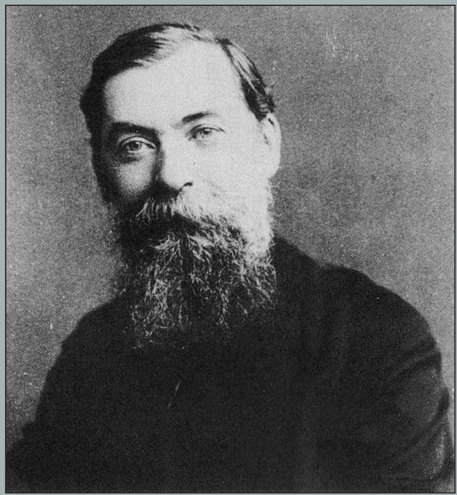
ALUMINUM
A RARE METAL BEFORE 1887

The 10 Most Abundant Elements in the Earth's Crust
Source: CRC Handbook of Chemistry and Physics, 77th Edition.

Element	Abundance percent by weight	Abundance parts per million by weight
Oxygen	46.1%	461,000
Silicon	28.2%	282,000
Aluminum	8.23%	82,300
Iron	5.63%	56,300
Calcium	4.15%	41,500
Sodium	2.36%	23,600
Magnesium	2.33%	23,300
Potassium	2.09%	20,900
Titanium	0.565%	5,650
Hydrogen	0.14%	1,400

Karl Joseph Bayer



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Chateau Des Beaux, France

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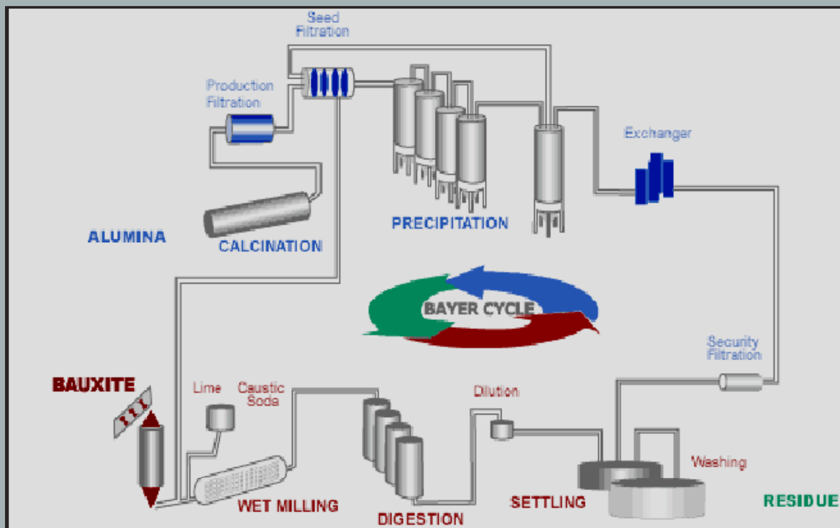
BAYER ALUMINA 1887 PROCESS



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Paul-Louis-Toussaint Héroult
(* April 10, 1863, + May 9, 1914)
Patent: April 23rd, 1886

Charles Martin Hall
(* Dec. 6, 1863, + Dec. 27, 1914)
Patent: July 9th, 1886

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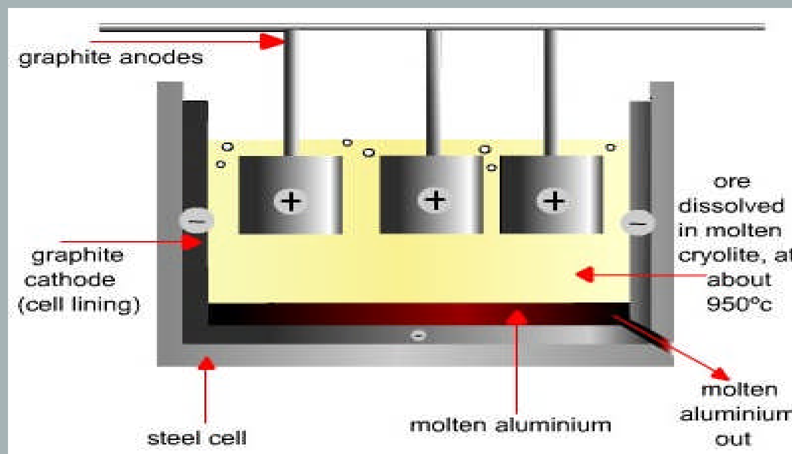
Electrometallurgy

Hall – Heroult Aluminum Process 1887



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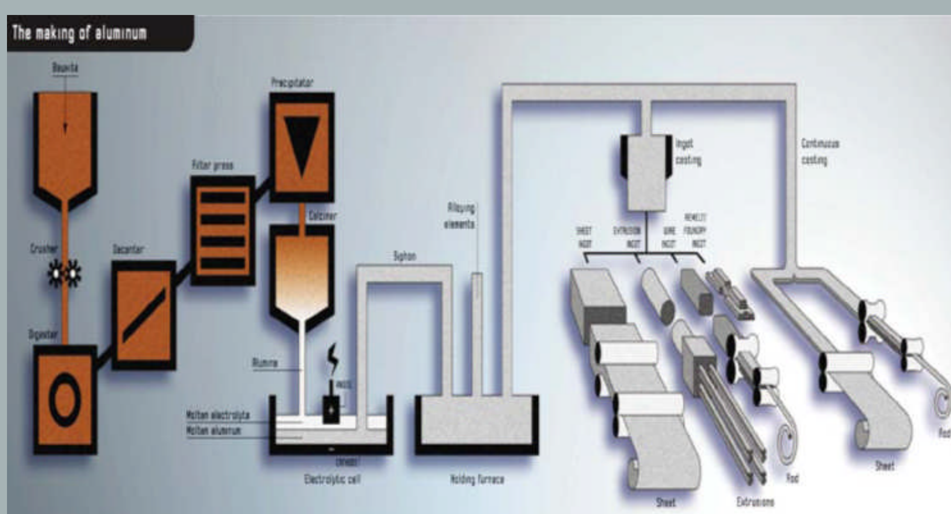
ALUMINUM



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ALUMINUM
A COMMON METAL AFTER 1887

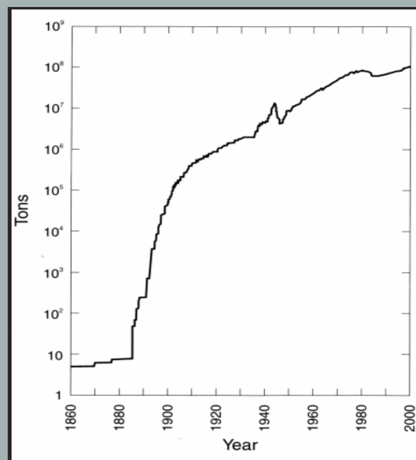

Figure 10.1: Tonnage of bauxite treated annually.

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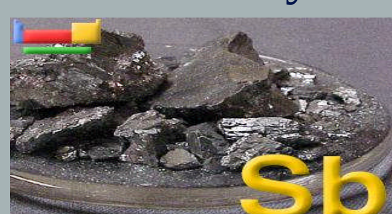
CRITICAL MATERIALS
Rare Earths

Antimony



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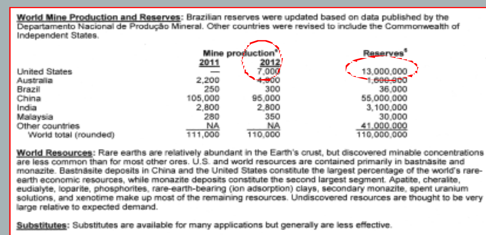
CRITICAL MATERIALS

Rare Earths



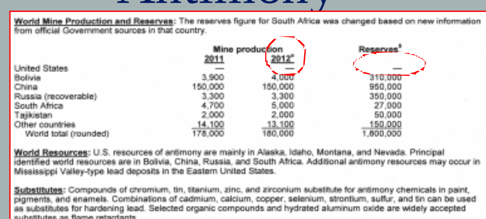
World Mine Production and Reserves: Brazilian reserves were updated based on data published by the Departamento Nacional de Produção Mineral. Other countries were revised to include the Commonwealth of Independent States.

	Mine production[e] 2011	Mine production[e] 2012	Reserves[5]
United States	—	7,000	13,000,000
Australia	2,200	4,000	1,600,000
Brazil	250	300	36,000
China	105,000	95,000	55,000,000
India	2,800	2,800	3,100,000
Malaysia	280	350	30,000
Other countries	NA	NA	41,000,000
World total (rounded)	111,000	110,000	110,000,000

World Resources: Rare earths are relatively abundant in the Earth's crust, but discovered minable concentrations are less common than for most other ores. U.S. and world resources are contained primarily in bastnäsite and monazite. Bastnäsite deposits in China and the United States constitute the largest percentage of the world's rare-earth economic resources, while monazite deposits constitute the second largest segment. Apatite, cheralite, eudialyte, loparite, phosphorites, rare-earth-bearing (ion adsorption) clays, secondary monazite, spent uranium solutions, and xenotime make up most of the remaining resources. Undiscovered resources are thought to be very large relative to expected demand.

Substitutes: Substitutes are available for many applications but generally are less effective.

Antimony



World Mine Production and Reserves: The reserves figure for South Africa was changed based on new information from official Government sources in that country.

	Mine production 2011	Mine production 2012[e]	Reserves[5]
United States	—	—	—
Bolivia	3,900	4,000	310,000
China	150,000	150,000	950,000
Russia (recoverable)	3,300	3,300	350,000
South Africa	4,700	5,000	27,000
Tajikistan	2,000	2,000	50,000
Other countries	14,100	13,100	150,000
World total (rounded)	178,000	180,000	1,800,000

World Resources: U.S. resources of antimony are mainly in Alaska, Idaho, Montana, and Nevada. Principal identified world resources are in Bolivia, China, Russia, and South Africa. Additional antimony resources may occur in Mississippi Valley-type lead deposits in the Eastern United States.

Substitutes: Compounds of chromium, tin, titanium, zinc, and zirconium substitute for antimony chemicals in paint, pigments, and enamels. Combinations of cadmium, calcium, copper, selenium, strontium, sulfur, and tin can be used as substitutes for hardening lead. Selected organic compounds and hydrated aluminum oxide are widely accepted substitutes as flame retardants.

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REE USES

As of 2009, the USGS reports the distribution of rare earths by end use, in decreasing order, was:

- *chemical catalysts 22%*
- *metallurgical applications and alloys 21%*
- *petroleum refining catalysts 14%*
- *automotive catalytic converters 13%*
- *glass polishing and ceramics 9%*
- *rare earth phosphors for computer monitors, lighting, televisions 8%*
- *permanent magnets 7%*
- *electronics 3%*
- *others 3 %*

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Rare Earths

- ***Total TREO abundance in earth is 220 ppm. Carbon 200 ppm !***
- ***They are widely distributed in low individual concentrations but found all together normally.***
- ***There are 123 important rare earth deposits in the world and they are located in twenty countries.***
- ***They occur in over 200 minerals.***
- ***95% of TREOs occur in the minerals bastansite, monazite and xenotime.***

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Rare Earths

Powderhorn White Earth Deposit
Gunnison, Colorado - Perovskite, $CaTiO_3$

500 Million Tons of 8% Perovskite - 0.36% TREO !
Development (hence rarity) of Ti and TREO impeded by concentration and separation not availability !

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Example Flow Sheet – Mineral Processing – Flotation and Chemical Treatment

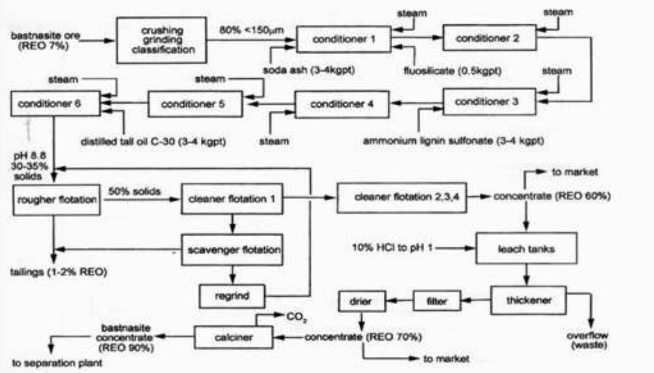

Figure 3.9 Simplified flowsheet for the recovery of bastnasite at the Molycorp plant (Aplan 1988).

A very complex flow sheet that requires significant energy and chemicals. Research may lead to alternative surface chemistry and flotation processes.

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Rare Earths Hydrometallurgy

- ***Rare earths are difficult to separate as they have very similar chemical natures.***

- ***Took 160 years for scientists to isolate and identify all of them.***

- ***They have 'lanthanide contraction' which is the root cause of rare earth chemistry similarities.***

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Rare Earths Hydrometallurgy

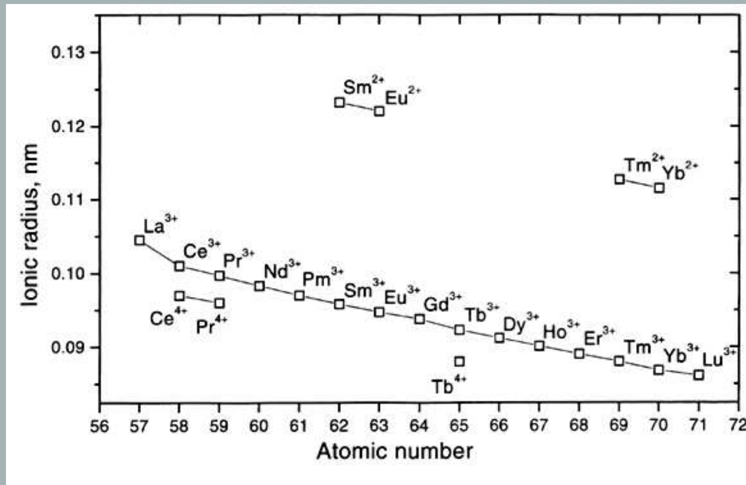

Figure 1.2 Lanthanide contraction.

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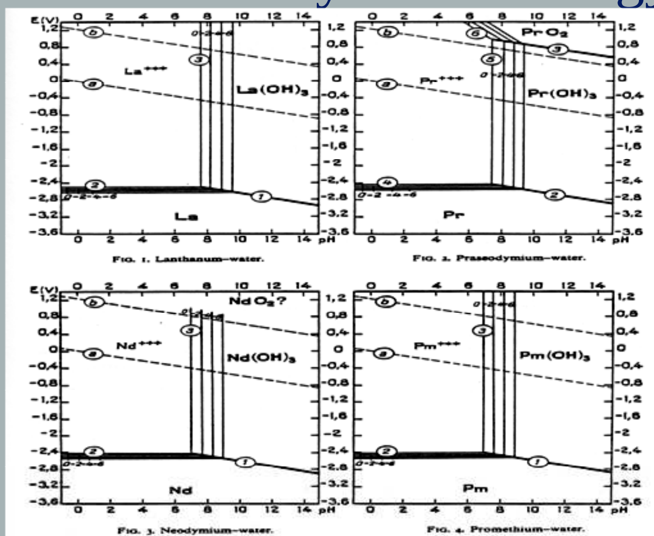
Rare Earths Hydrometallurgy



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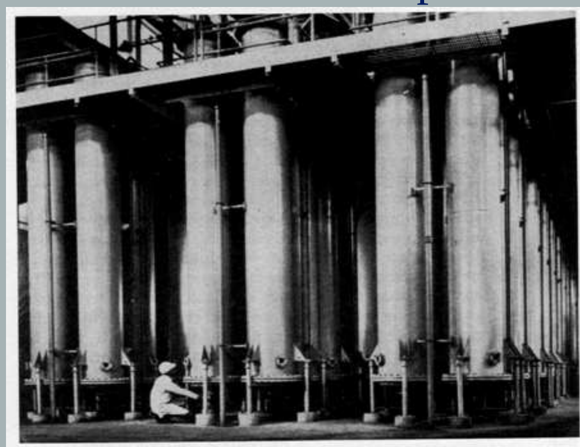
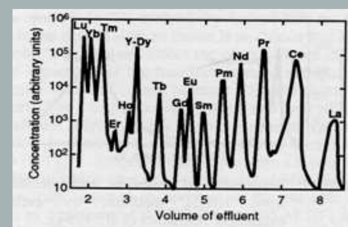
Selective Hydrometallurgical IX Separation of REO



Ion Exchange Columns for the Separation of the Lanthanides at Michigan Chemical Corporation, St. Louis Michigan.

Rare earth oxide	Yield (%)	Purity (%)
Er_2O_3	82	99.9
Yb_2O_3	50	99.9
Tm_2O_3	86	97
Ho_2O_3	66	98
$Dy_2O_3 + Y_2O_3$	Not high	99.9

Typical Yields and Purities Of The Rare Earth Oxides Recovered Through Ion Exchange.



Separation of the Lanthanides from Cationic Exchanger DOWEX 50 with 1 M Lactate pH = 3.19, flow rate at 0.4 ml/cm2/min.

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Extraction of REO from Bastnasite

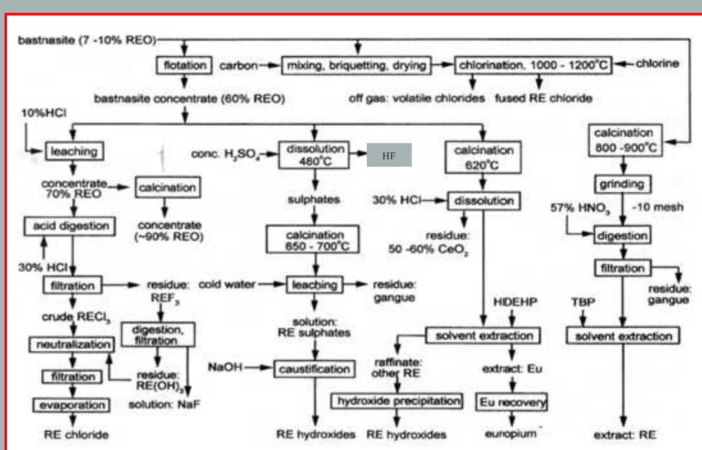

Figure 3.15 Chemical processing of bastnasite.

Once a concentrate is obtained, then the metals of interest must be extracted from the material. Several approaches are possible, usually involving calcining and acid leaching.

The solutions are then subjected to ion exchange or solvent extraction for purification.

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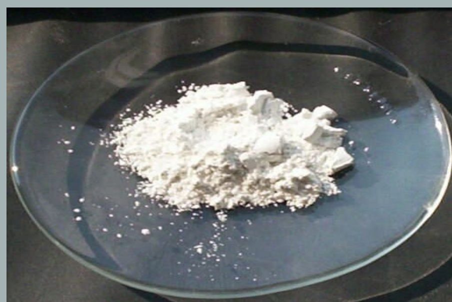
ANTIMONY



Antimony History

- Known in 4000 B.C.
- Metal known as regulus
- Greek for “metal not found alone”
- Metal is brittle - must be alloyed
- Early 1900’s used in munitions
- Automobile batteries boosted usage
- Flame retardants now major use

Antimony Occurrence and Mineralogy

- Abundance in earth 0.2 g/t
- Antimony is a chalcophile
- Over 100 Antimony minerals are known
- Stibnite, Sb_2S_3, is the predominant ore

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ANTIMONY

Table 1. Common Primary Antimony Minerals.

Horsfordite Cu_6Sb	Dyscrasite Ag_3Sb	Stibiodomeykite $Cu_3(As,Sb)$
Aurostibite $AuSb_2$	Breithauptite NiSb	Arite Ni(As,Sb)
Ullmannite NiSbS	Gudmundite FeSbS	Stibnite Sb_2S_3
Stibiobismuthine $(Bi,Sb)_4S_7$	Tetrahedrite $Cu_{12}Sb_4S_{13}$	Annivite $Cu_{12}(Sb,Bi,As)_4S_{13}$
Freibergite $(Cu,Ag)_{12}Sb_4S_{13}$	Bournonite $PbCuSbS_3$	Stephanite Ag_5SbS_4
Ramdohrite $Ag_2Pb_3Sb_3S_9$	Andorite $AgPbSb_3S_6$	Geocronite $Pb5(As,Sb)_{12}S_8$
Zinckenite $PbSb_2S_4$	Jamesonite, $Pb_4FeSb_6S_{14}$	Boulangerite $Pb_5Sb_4S_{11}$
Falkmanite $Pb_3Sb_2S_6$	Meneghihite $Pb_4Sb_2S_7$	Cylindrite $Pb_3Sn_4Sb_2S_{14}$
Franckeite $Pb_5Sn_3Sb_2S_{14}$	Livingstonite $HgSb_4S_7$	Berthierite $FeSb_2S_4$
Famatinite Cu_3SbS_4	Stibioluzonite $Cu_3(Sb,As)S_4$	Berthonite $Cu_7Pb_2Sb_5S_{13}$
Bolivianite $Ag_2Sb_{12}S_{19}$	Sulfo-antimonite $Ag_2Pb_7Sb_8S_{20}$	Kermisite Sb_2S_2O
Stibiotantalite $SbTaO_4$	Stibiocolumbite $SbNbO_4$	Senarmontite Sb_2O_3
Romeite $5CaO:3Sb_2O_5$	Stibiconite $Sb_2O_4:H_2O$	Stenhuggarite $CaFeSbAs_2O_7$
Cervantite Sb_2O_4	Stibio-tellurobismutite $B_{11}0SbTe_7$	Valentinite Sb_2O_3

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Antimony Uses and Applications

- Sb_2O_3 for flame retardants, pigments, and catalysts.
- $NaSb(OH)_6$ for flame retardants and glass.
- Antimonial lead and alloys.
- Sb_2S_3 in brake lines and matches.
- Sb_2O_5 for flame retardants.

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Antimony

For optical rewritable disks like DVD as a material to phase-change layer providing increase of data capacity

For low-noise refrigerators and wine cellars of recent advanced models as a mixture to materials of thermoelectric module of cooling system.

For its flame retardant properties, antimony is used as an additive in the production of components for office electronic equipment such as personal computers, copying and facsimile machines For electronic components such as IC filler and IC chips, as a flame retardant.

For electronic components such as IC filler and IC chips, as a flame retardant additive.

For polyester fiber as a polymerization catalyst.

For components of automobile such as an engine block as additives in molding and a brake pad/lining as additives for friction material, for wire coating materials,rubber materials and for the plastics in automobile interiors for its flame retardant properties.

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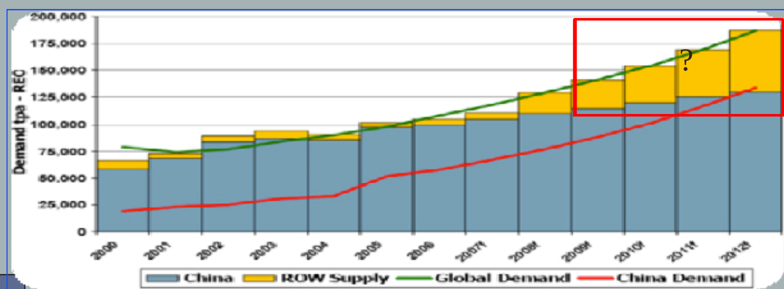
ANTIMONY

Antimony Market Factors

Global Demand is increasing as the:

Chinese economy continues to grow at approximately 10% per year;

And the Western world is increasing the requirements on fire-proofing.



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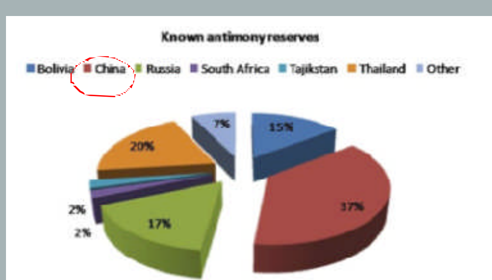
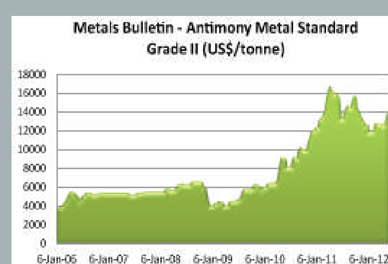
Worldwide known reserves are be only 2.1m tonne of Sb metal.
This represents ***only 11 years*** of consumption left.





China has the majority of known metal reserves.
Antimony (Sb – stibnite) is a very scarce mineral

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Economics of Antimony

Few Published Prices

Chinese Dominate for Past 25 Years

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Zhao Tian Cong

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ANTIMONY

Typical Stibnite Ore Mineral Processing Results

Operation	Ore Grade, % Sb	Conc. Grade, % Sb	Tails Grade, % Sb	Recovery, %
Hand sorting	2.25	7.80	0.12	95.95
Heavy media	1.58	2.65	0.18	95.11
Flotation	3.19	47.58	0.21	93.97
Average	2.68	19.44	0.18	94.11

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Pyrometallurgy of Antimony

- Generally grade determines process
- 5 - 25% Sb - volatilized to Sb_2O_3
- 25 - 40% Sb - smelted in blast furnace
- 45 - 60% Sb - liquation or iron precipitation

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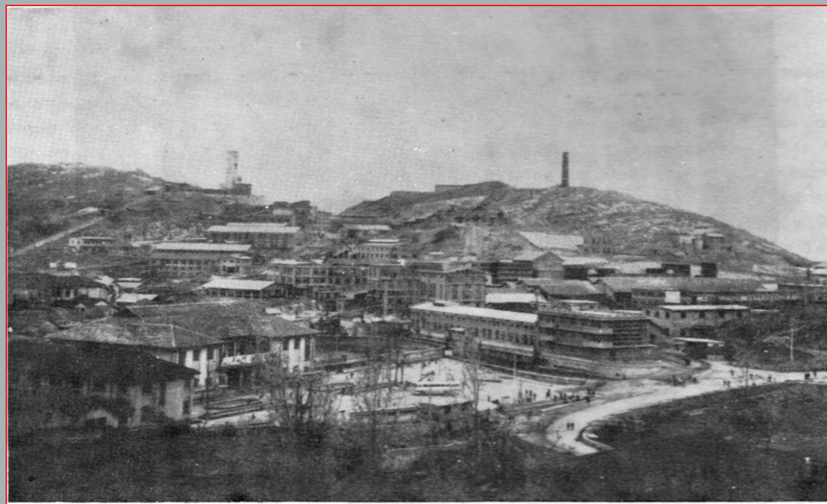

The north mining, ore-dressing and smelting division of Xikuangshan Antimony Complex.

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Hydrometallurgy of Antimony

- Alkaline Sulfide system
- Acidic Chloride system

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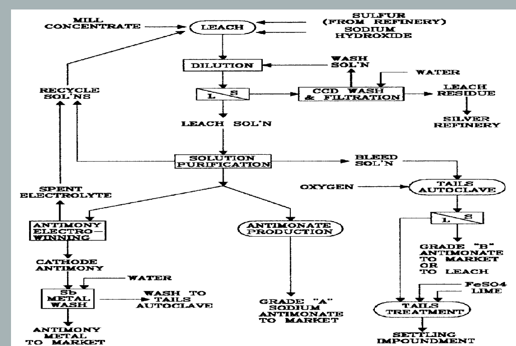
Sunshine Antimony Process



CRITICAL ASPECT OF CRITICAL MATERIALS

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CRITICAL ASPECT OF CRITICAL MATERIALS

- 50 % of All Experienced North American Mineral Engineering Expertise Will Retire In Less Than 10 Years.
- In North America Only About A Half Dozen Schools Teach Or Do Research In Extractive Metallurgy.
- No North American School Offers An Accredited Distinct Mineral Processing Or Extractive Metallurgy Degree.

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CRITICAL ASPECT OF CRITICAL MATERIALS

- There Is Only One Disticnt Metallurgical Engineering Program In North America (U of Utah). The Rest Are Aligned With Or Subsets Of Materials Or Other Programs.
- We Have Lost 3 Generations of Mineral Engineering Talent.
- We Lost The US Bureau of Mines.

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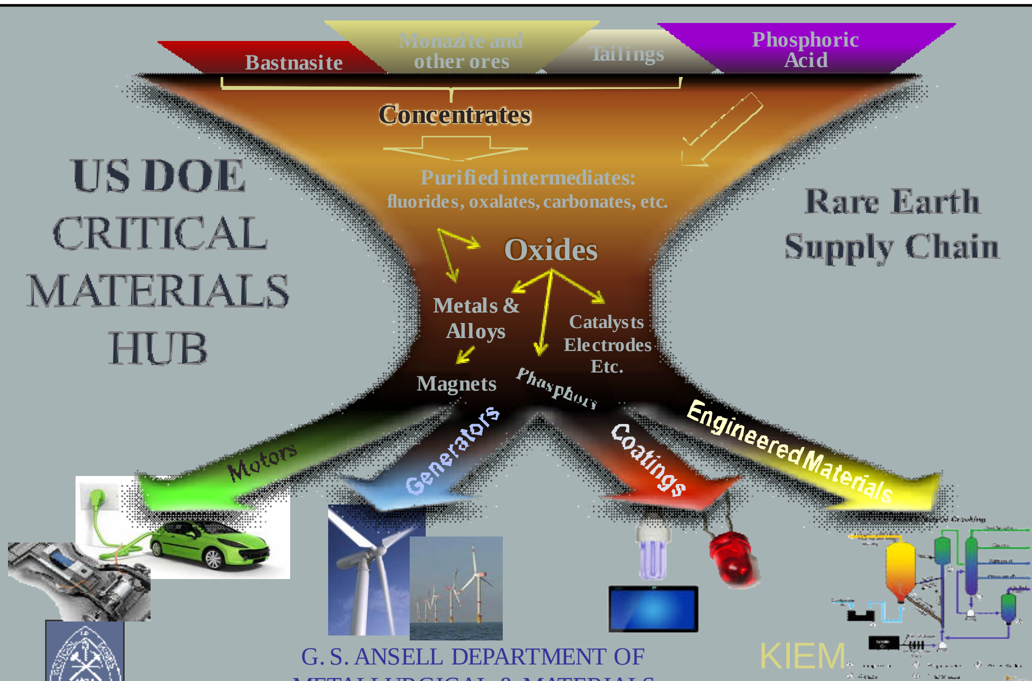
CRITICAL ASPECT OF CRITICAL MATERIALS

- We Cannot Attract, Hire Or Retain Qualified Faculty.
- The Western Australia School of Mines Just Consolidated Mining Engineering With Extractive Metallurgy.
- The Camborne School of Mines Just Suspended It's Mineral Engineering Program.
- We Gave Up Our Mineral Engineering Intellectual Capacity And It Will Take A Long Time And A Lot of Effort To Regain It.



CMI

Accelerating Energy Innovations

Critical Materials Institute

AN ENERGY INNOVATION HUB

U.S. DEPARTMENT OF ENERGY

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Two Guiding Principles

- Produce more

- *Use less*

- We have to address the entire materials lifecycle, going from birth through death, and beyond, to include resurrection.

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Critical Materials Institute

Projects at Colorado School of Mines

- *Project 1.1.1: Advanced Beneficiation Techniques*
- *Project 1.2.2: Conversion to Metals, Alloys and Materials*
- *Project 2.1.4: Thermomagnetic Processing of Rare Earth Magnets*
- *Project 3.1.1: Recovery and Reuse of Rare Earth Metals from Phosphor Dusts*
- *Project 3.1.3: Cost Effective Recycling of Rare Earth Containing Magnets*
- *Project 3.1.4: Beneficiation of Photovoltaic (and other) Functional Coatings*
- *Project 4.2.1: Treatment of mineral processing waste streams and recovery of clean water using microfiltration systems*
- *Project 4.3.1: Criticality and sustainability assessment*
- *Project 4.3.2: Economic analysis of CMI research and global material supply chains*

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Caelen Anderson is a PhD student. His research involves the Surface Chemistry of Rare Earth Minerals with Dr. Taylor.

Matt Esquibel is a MS student. His research is on the recycling of indium and rare earths from plasma display panels (flat-panel displays) with Dr. Taylor.

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Daniel Haughey, MS student working on rare earth recovery from thermal spray wastes with Dr. Taylor.

Ben Kronholm, MS student working on TREO ion exchange with Dr. Anderson.

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Patrick Eduafo MS student working on Rare Earth Recovery from Fluorescent lights with Dr. Mishra.

James Wright MS student working on Rare Earth Recovery from magnets lights with Dr. Taylor.

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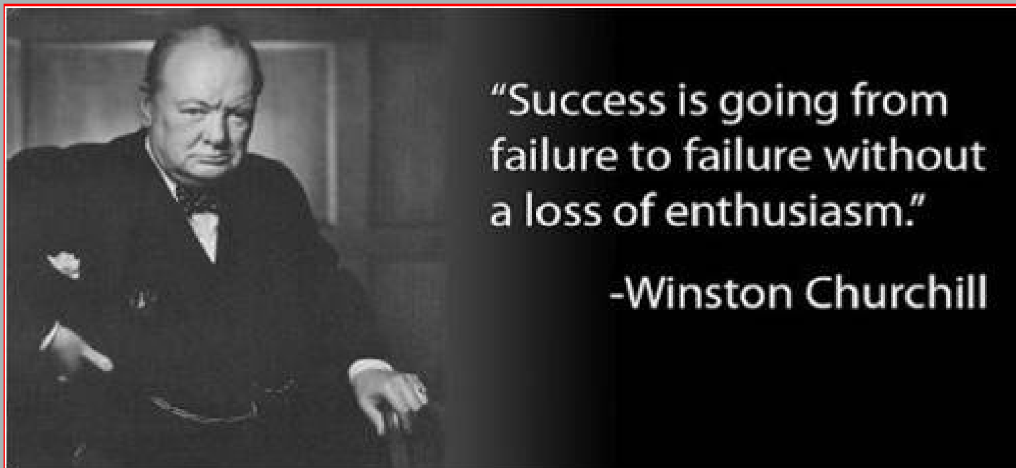
Metallurgical Innovation Philosophy



Thank You For This Opportunity to Present!

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QUESTIONS

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If you want a copy of the presentation please give me a business card or email me at cganders@mines.edu

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Monazite

Bastnasite

SEPARATION SCIENCE AND TECHNOLOGY EDUCATION: EXTRACTIVE METALLURGY PERSPECTIVE

Dr. Corby G. Anderson
Harrison Western Professor

The Kroll Institute for Extractive Metallurgy
Colorado School of Mines

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