Molten-Salt Electrolysis:

Industrial Applications and Outlook

Jonathan “Jo” Melville
CSP Strategy Meeting
December 2nd, 2021

SOLAR ENERGY TECHNOLOGIES OFFICE
U.S. Department Of Energy

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Redox Reactions: A Primer

- Refining metals = bringing them to +0 oxidation state
  - Metals in ores exist as oxidized species
- Changing oxidation state is definitionally redox
  - Refining ores to metals requires a reducing agent

Redox Reactions: A Primer

- Refining metals = bringing them to +0 oxidation state
  - Metals in ores exist as oxidized species
- Changing oxidation state is definitionally redox
  - Refining ores to metals requires a reducing agent

$$Fe_2O_3 + 3\ CO \rightarrow 2\ Fe + 3\ CO_2$$

Redox Reactions: A Primer

- Refining metals = bringing them to +0 oxidation state
  - Metals in ores exist as oxidized species
- Changing oxidation state is definitionally redox
  - Refining ores to metals requires a reducing agent

$$\overset{+3}{Fe_2}O_3 + 3\,\underset{+2}{C}O \rightarrow 2\,\overset{0}{Fe} + 3\,\underset{+4}{C}O_2$$

Redox Reactions: A Primer

- Refining metals = bringing them to +0 oxidation state
  - Metals in ores exist as oxidized species
- Changing oxidation state is definitionally redox
  - Refining ores to metals requires a reducing agent

$$\overbrace{\overset{+3}{Fe}_2O_3 + 3\,\underset{+2}{C}O \rightarrow 2\,\overset{0}{Fe}}^{\text{reduced by 3 } e^- \text{ / atom}} + 3\,\underset{+4}{C}O_2$$

Redox Reactions: A Primer

- Refining metals = bringing them to +0 oxidation state
  - Metals in ores exist as oxidized species
- Changing oxidation state is definitionally redox
  - Refining ores to metals requires a reducing agent

reduced by 3 e^- / atom

$$\overset{+3}{Fe_2O_3} + 3\,\overset{+2}{CO} \rightarrow 2\,\overset{0}{Fe} + 3\,\overset{+4}{CO_2}$$

oxidized by 2 e^- / atom

Redox Reactions: A Primer

- Refining metals = bringing them to +0 oxidation state
  - Metals in ores exist as oxidized species
- Changing oxidation state is definitionally redox
  - Refining ores to metals requires a reducing agent

reduced by 3 e^- / atom

$$\overset{+3}{Fe}_2O_3 + 3\,\overset{+2}{C}O \rightarrow 2\,\overset{0}{Fe} + 3\,\overset{+4}{C}O_2$$

oxidized by 2 e^- / atom

carbothermic reduction

Redox Reactions: A Primer

- Refining metals = bringing them to +0 oxidation state
    - Metals in ores exist as oxidized species
- Changing oxidation state is definitionally redox
    - Refining ores to metals requires a reducing agent

reduced by 3 e^- / atom

$$\overset{+3}{Fe}_2O_3 + 3\,\underset{0}{H}_2 \rightarrow 2\,\overset{0}{Fe} + 3\,\underset{+1}{H}_2O$$

oxidized by 1 e^- / atom

hydrogenic reduction

Redox Reactions: A Primer

- Refining metals = bringing them to +0 oxidation state
  - Metals in ores exist as oxidized species
- Changing oxidation state is definitionally redox
  - Refining ores to metals requires a reducing agent

reduced by 3 e^- / atom

$$\overset{+3}{Fe}_2O_3 + 2\,\underset{0}{Al} \rightarrow 2\,\overset{0}{Fe} + \underset{+3}{Al}_2O_3$$

oxidized by 3 e^- / atom

aluminothermic reduction


23

Redox Reactions: A Primer

- Refining metals = bringing them to +0 oxidation state
  - Metals in ores exist as oxidized species
- Changing oxidation state is definitionally redox
  - Refining ores to metals requires a reducing agent

reduced by 3 e^- / atom

$$\overset{+3}{\mathrm{Fe}}_2\mathrm{O}_3 + 2\,\underset{0}{\mathrm{Al}} \rightarrow 2\,\overset{0}{\mathrm{Fe}} + \underset{+3}{\mathrm{Al}}_2\mathrm{O}_3$$

oxidized by 3 e^- / atom

aluminothermic reduction

Redox Reactions: A Primer

- Refining metals = bringing them to +0 oxidation state
  - Metals in ores exist as oxidized species
- Changing oxidation state is definitionally redox
  - Refining ores to metals requires a reducing agent
- Electrolysis is just redox where half-reactions are separated and electrons are your reducing agent

Redox Reactions: A Primer

- Refining metals = bringing them to +0 oxidation state
  - Metals in ores exist as oxidized species
- Changing oxidation state is definitionally redox
  - Refining ores to metals requires a reducing agent
- Electrolysis is just redox where half-reactions are separated and electrons are your reducing agent

Redox Reactions: A Primer

- Refining metals = bringing them to +0 oxidation state
  - Metals in ores exist as oxidized species
- Changing oxidation state is definitionally redox
  - Refining ores to metals requires a reducing agent
- Electrolysis is just redox where half-reactions are separated and electrons are your reducing agent

$$\overset{+3}{\mathrm{Fe}}_2\mathrm{O}_3 + 6\,e^- \rightarrow 2\,\overset{0}{\mathrm{Fe}} + 3\,\mathrm{O}^{2-}$$

Redox Reactions: A Primer

- Refining metals = bringing them to +0 oxidation state
  - Metals in ores exist as oxidized species
- Changing oxidation state is definitionally redox
  - Refining ores to metals requires a reducing agent
- Electrolysis is just redox where half-reactions are separated and electrons are your reducing agent

reduced by 3 e^- / atom

$$\overset{+3}{Fe}_2O_3 + 6\,e^- \rightarrow 2\,\overset{0}{Fe} + 3\,O^{2-}$$

Redox Reactions: A Primer

- Refining metals = bringing them to +0 oxidation state
  - Metals in ores exist as oxidized species
- Changing oxidation state is definitionally redox
  - Refining ores to metals requires a reducing agent
- Electrolysis is just redox where half-reactions are separated and electrons are your reducing agent

$$\overbrace{\overset{+3}{Fe}_2O_3 + 6\,e^- \rightarrow 2\,\overset{0}{Fe}}^{\text{reduced by 3 } e^- \text{ / atom}} + 3\,O^{2-}$$

$$3\,\underset{-2}{O^{2-}} \rightarrow 3/2\,\underset{0}{O}_2 + 6\,e^-$$

Redox Reactions: A Primer

- Refining metals = bringing them to +0 oxidation state
  - Metals in ores exist as oxidized species
- Changing oxidation state is definitionally redox
  - Refining ores to metals requires a reducing agent
- Electrolysis is just redox where half-reactions are separated and electrons are your reducing agent

reduced by 3 e^- / atom

$$\overset{+3}{Fe}_2O_3 + 6\,e^- \rightarrow 2\,\overset{0}{Fe} + 3\,O^{2-}$$

$$3\,\underset{-2}{O}^{2-} \rightarrow 3/2\,\underset{0}{O}_2 + 6\,e^-$$

oxidized by 2 e^- / atom

Redox Reactions: A Primer

- Refining metals = bringing them to +0 oxidation state
  - Metals in ores exist as oxidized species
- Changing oxidation state is definitionally redox
  - Refining ores to metals requires a reducing agent
- Electrolysis is just redox where half-reactions are separated and electrons are your reducing agent

reduced by 3 e^- / atom

$$\overset{+3}{Fe}_2\underset{-2}{O}_3 \rightarrow 2\ \overset{0}{Fe} + 3/2\ \underset{0}{O}_2$$

oxidized by 2 e^- / atom

Electrolysis and You: A Primer

electro + *lysis*: “to break apart with electricity”

Anode: electrode where oxidation takes place

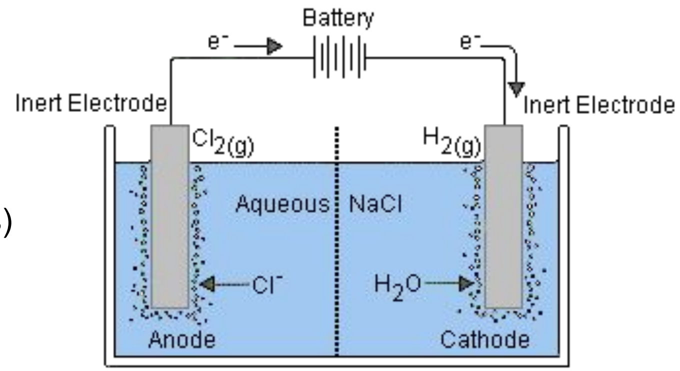
↳ **Oxidation:** an increase in charge state (more positive; loss of electrons)

Cathode: electrode where reduction takes place

↳ **Reduction:** a decrease in charge state (more negative; gain of electrons)

Electrolyte: conductive solvent mediating electron/ion transfer between cathode and anode

Decomposition potential: minimum applied EMF needed to induce electrolysis; $E^\circ_{\mathrm{cell}} = E^\circ_{\mathrm{red}} - E^\circ_{\mathrm{ox}}$



Electrolysis and You: A Primer

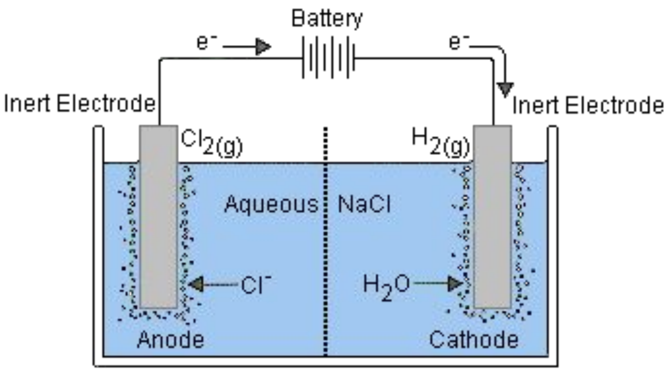
Electrolyte: aqueous NaCl (~26% w/w solution)

Anode: titanium mixed-metal oxide

↳ **Oxidation half-reaction:** $2\ Cl^- \rightarrow Cl_2 + 2\ e^-$ ($E°$ = 1.23 V)

Cathode: graphite

↳ **Reduction half-reaction:** $2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$ ($E°$ = -0.99 V)



Chloralkali process

Net Rxn:

reduced by 1 e⁻ / atom

$$2\ Na\underset{-1}{Cl} + 2\ \overset{+1}{H}_2O \rightarrow 2\ NaOH + \underset{0}{Cl}_2 + \overset{0}{H}_2 \quad (E° = -2.23\ V)$$

oxidized by 1 e⁻ / atom

Appl. Sci. **2019**, *9*, 284.

The Reactivity Series

The Reactivity Series

Metal	Ion	Reactivity	Extraction
Caesium Cs	Cs^{+}	reacts with cold water	electrolysis
Rubidium Rb	Rb^{+}		
Potassium K	K^{+}		
Sodium Na	Na^{+}		
Lithium Li	Li^{+}		
Radium Ra	Ra^{2+}		
Barium Ba	Ba^{2+}		
Strontium Sr	Sr^{2+}		
Calcium Ca	Ca^{2+}		
Magnesium Mg	Mg^{2+}	reacts very slowly with cold water, but rapidly in boiling water, and very vigorously with acids	
Beryllium Be	Be^{2+}	reacts with acids and steam	
Aluminium Al	Al^{3+}		
Titanium Ti	Ti^{4+}	reacts with concentrated mineral acids	pyrometallurgical extraction using magnesium, or less commonly other alkali metals, hydrogen or calcium in the Kroll process
Manganese Mn	Mn^{2+}	reacts with acids; very poor reaction with steam	smelting with coke
Zinc Zn	Zn^{2+}		
Chromium Cr	Cr^{3+}		aluminothermic reaction
Iron Fe	Fe^{2+}		smelting with coke
Cadmium Cd	Cd^{2+}		
Cobalt Co	Co^{2+}		
Nickel Ni	Ni^{2+}		
Tin Sn	Sn^{2+}		
Lead Pb	Pb^{2+}		
Antimony Sb	Sb^{3+}	may react with some strong oxidizing acids	heat or physical extraction
Bismuth Bi	Bi^{3+}		
Copper Cu	Cu^{2+}	reacts slowly with air	
Tungsten W	W^{3+}	may react with some strong oxidizing acids	
Mercury Hg	Hg^{2+}		
Silver Ag	Ag^{+}		
Gold Au	Au^{3+}[5][6]		
Platinum Pt	Pt^{4+}		

The Reactivity Series

Metal	Ion	Reactivity	Extraction
Caesium Cs	Cs^{+}	reacts with cold water	electrolysis
Rubidium Rb	Rb^{+}		
Potassium K	K^{+}		
Sodium Na	Na^{+}		
Lithium Li	Li^{+}		
Radium Ra	Ra^{2+}		
Barium Ba	Ba^{2+}		
Strontium Sr	Sr^{2+}		
Calcium Ca	Ca^{2+}		
Magnesium Mg	Mg^{2+}	reacts very slowly with cold water, but rapidly in boiling water, and very vigorously with acids	
Beryllium Be	Be^{2+}	reacts with acids and steam	
Aluminium Al	Al^{3+}		
Titanium Ti	Ti^{4+}	reacts with concentrated mineral acids	pyrometallurgical extraction using magnesium, or less commonly other alkali metals, hydrogen or calcium in the Kroll process
Manganese Mn	Mn^{2+}	reacts with acids; very poor reaction with steam	smelting with coke
Zinc Zn	Zn^{2+}		
Chromium Cr	Cr^{3+}		aluminothermic reaction
Iron Fe	Fe^{2+}		smelting with coke
Cadmium Cd	Cd^{2+}		
Cobalt Co	Co^{2+}		
Nickel Ni	Ni^{2+}		
Tin Sn	Sn^{2+}		
Lead Pb	Pb^{2+}		
Antimony Sb	Sb^{3+}	may react with some strong oxidizing acids	heat or physical extraction
Bismuth Bi	Bi^{3+}		
Copper Cu	Cu^{2+}	reacts slowly with air	
Tungsten W	W^{3+}	may react with some strong oxidizing acids	
Mercury Hg	Hg^{2+}		
Silver Ag	Ag^{+}		
Gold Au	Au^{3+}[5][6]		
Platinum Pt	Pt^{4+}		

INCREASING REACTIVITY

The Reactivity Series

Metal	Ion	Reactivity	Extraction
Caesium Cs	Cs^{+}	reacts with cold water	electrolysis
Rubidium Rb	Rb^{+}		
Potassium K	K^{+}		
Sodium Na	Na^{+}		
Lithium Li	Li^{+}		
Radium Ra	Ra^{2+}		
Barium Ba	Ba^{2+}		
Strontium Sr	Sr^{2+}		
Calcium Ca	Ca^{2+}		
Magnesium Mg	Mg^{2+}	reacts very slowly with cold water, but rapidly in boiling water, and very vigorously with acids	
Beryllium Be	Be^{2+}	reacts with acids and steam	
Aluminium Al	Al^{3+}		
Titanium Ti	Ti^{4+}	reacts with concentrated mineral acids	pyrometallurgical extraction using magnesium, or less commonly other alkali metals, hydrogen or calcium in the Kroll process
Manganese Mn	Mn^{2+}	reacts with acids; very poor reaction with steam	smelting with coke
Zinc Zn	Zn^{2+}		
Chromium Cr	Cr^{3+}		aluminothermic reaction
Iron Fe	Fe^{2+}		smelting with coke
Cadmium Cd	Cd^{2+}		
Cobalt Co	Co^{2+}		
Nickel Ni	Ni^{2+}		
Tin Sn	Sn^{2+}		
Lead Pb	Pb^{2+}		
Antimony Sb	Sb^{3+}	may react with some strong oxidizing acids	heat or physical extraction
Bismuth Bi	Bi^{3+}		
Copper Cu	Cu^{2+}	reacts slowly with air	
Tungsten W	W^{3+}	may react with some strong oxidizing acids	
Mercury Hg	Hg^{2+}		
Silver Ag	Ag^{+}		
Gold Au	Au^{3+}[5][6]		
Platinum Pt	Pt^{4+}		

INCREASING REACTIVITY

$E° = +1.52\ V$

The Reactivity Series

Metal	Ion	Reactivity	Extraction
Caesium Cs	Cs^{+}	reacts with cold water	electrolysis
Rubidium Rb	Rb^{+}		
Potassium K	K^{+}		
Sodium Na	Na^{+}		
Lithium Li	Li^{+}		
Radium Ra	Ra^{2+}		
Barium Ba	Ba^{2+}		
Strontium Sr	Sr^{2+}		
Calcium Ca	Ca^{2+}		
Magnesium Mg	Mg^{2+}	reacts very slowly with cold water, but rapidly in boiling water, and very vigorously with acids	
Beryllium Be	Be^{2+}	reacts with acids and steam	
Aluminium Al	Al^{3+}		
Titanium Ti	Ti^{4+}	reacts with concentrated mineral acids	pyrometallurgical extraction using magnesium, or less commonly other alkali metals, hydrogen or calcium in the Kroll process
Manganese Mn	Mn^{2+}	reacts with acids; very poor reaction with steam	smelting with coke
Zinc Zn	Zn^{2+}		
Chromium Cr	Cr^{3+}		aluminothermic reaction
Iron Fe	Fe^{2+}		smelting with coke
Cadmium Cd	Cd^{2+}		
Cobalt Co	Co^{2+}		
Nickel Ni	Ni^{2+}		
Tin Sn	Sn^{2+}		
Lead Pb	Pb^{2+}		
Antimony Sb	Sb^{3+}	may react with some strong oxidizing acids	heat or physical extraction
Bismuth Bi	Bi^{3+}		
Copper Cu	Cu^{2+}	reacts slowly with air	
Tungsten W	W^{3+}	may react with some strong oxidizing acids	
Mercury Hg	Hg^{2+}		
Silver Ag	Ag^{+}		
Gold Au	Au^{3+}[5][6]		
Platinum Pt	Pt^{4+}		

INCREASING REACTIVITY

E° = +1.52 V

The Reactivity Series

Metal	Ion	Reactivity	Extraction
Caesium Cs	Cs^{+}	reacts with cold water	electrolysis
Rubidium Rb	Rb^{+}		
Potassium K	K^{+}		
Sodium Na	Na^{+}		
Lithium Li	Li^{+}		
Radium Ra	Ra^{2+}		
Barium Ba	Ba^{2+}		
Strontium Sr	Sr^{2+}		
Calcium Ca	Ca^{2+}		
Magnesium Mg	Mg^{2+}	reacts very slowly with cold water, but rapidly in boiling water, and very vigorously with acids	
Beryllium Be	Be^{2+}	reacts with acids and steam	
Aluminium Al	Al^{3+}		
Titanium Ti	Ti^{4+}	reacts with concentrated mineral acids	pyrometallurgical extraction using magnesium, or less commonly other alkali metals, hydrogen or calcium in the Kroll process
Manganese Mn	Mn^{2+}	reacts with acids; very poor reaction with steam	smelting with coke
Zinc Zn	Zn^{2+}		
Chromium Cr	Cr^{3+}		aluminothermic reaction
Iron Fe	Fe^{2+}		smelting with coke
Cadmium Cd	Cd^{2+}		
Cobalt Co	Co^{2+}		
Nickel Ni	Ni^{2+}		
Tin Sn	Sn^{2+}		
Lead Pb	Pb^{2+}		
Antimony Sb	Sb^{3+}	may react with some strong oxidizing acids	heat or physical extraction
Bismuth Bi	Bi^{3+}		
Copper Cu	Cu^{2+}	reacts slowly with air	
Tungsten W	W^{3+}	may react with some strong oxidizing acids	
Mercury Hg	Hg^{2+}		
Silver Ag	Ag^{+}		
Gold Au	Au^{3+}[5][6]		
Platinum Pt	Pt^{4+}		

INCREASING REACTIVITY

$E° = +1.52\ V$

The Reactivity Series

Metal	Ion	Reactivity	Extraction
Caesium Cs	Cs^{+}	reacts with cold water	electrolysis
Rubidium Rb	Rb^{+}		
Potassium K	K^{+}		
Sodium Na	Na^{+}		
Lithium Li	Li^{+}		
Radium Ra	Ra^{2+}		
Barium Ba	Ba^{2+}		
Strontium Sr	Sr^{2+}		
Calcium Ca	Ca^{2+}		
Magnesium Mg	Mg^{2+}	reacts very slowly with cold water, but rapidly in boiling water, and very vigorously with acids	
Beryllium Be	Be^{2+}	reacts with acids and steam	
Aluminium Al	Al^{3+}		
Titanium Ti	Ti^{4+}	reacts with concentrated mineral acids	pyrometallurgical extraction using magnesium, or less commonly other alkali metals, hydrogen or calcium in the Kroll process
Manganese Mn	Mn^{2+}	reacts with acids; very poor reaction with steam	smelting with coke
Zinc Zn	Zn^{2+}		
Chromium Cr	Cr^{3+}		aluminothermic reaction
Iron Fe	Fe^{2+}		smelting with coke
Cadmium Cd	Cd^{2+}		
Cobalt Co	Co^{2+}		
Nickel Ni	Ni^{2+}		
Tin Sn	Sn^{2+}		
Lead Pb	Pb^{2+}		
Antimony Sb	Sb^{3+}	may react with some strong oxidizing acids	heat or physical extraction
Bismuth Bi	Bi^{3+}		
Copper Cu	Cu^{2+}	reacts slowly with air	
Tungsten W	W^{3+}	may react with some strong oxidizing acids	
Mercury Hg	Hg^{2+}		
Silver Ag	Ag^{+}		
Gold Au	Au^{3+}[5][6]		
Platinum Pt	Pt^{4+}		

INCREASING REACTIVITY

$E° = -2.71$ V

The Reactivity Series

Metal	Ion	Reactivity	Extraction
Caesium Cs	Cs^+	reacts with cold water	electrolysis
Rubidium Rb	Rb^+		
Potassium K	K^+		
Sodium Na	Na^+		
Lithium Li	Li^+		
Radium Ra	Ra^{2+}		
Barium Ba	Ba^{2+}		
Strontium Sr	Sr^{2+}		
Calcium Ca	Ca^{2+}		
Magnesium Mg	Mg^{2+}	reacts very slowly with cold water, but rapidly in boiling water, and very vigorously with acids	
Beryllium Be	Be^{2+}	reacts with acids and steam	
Aluminium Al	Al^{3+}		
Titanium Ti	Ti^{4+}	reacts with concentrated mineral acids	pyrometallurgical extraction using magnesium, or less commonly other alkali metals, hydrogen or calcium in the Kroll process
Manganese Mn	Mn^{2+}	reacts with acids; very poor reaction with steam	smelting with coke
Zinc Zn	Zn^{2+}		
Chromium Cr	Cr^{3+}		aluminothermic reaction
Iron Fe	Fe^{2+}		smelting with coke
Cadmium Cd	Cd^{2+}		
Cobalt Co	Co^{2+}		
Nickel Ni	Ni^{2+}		
Tin Sn	Sn^{2+}		
Lead Pb	Pb^{2+}		
Antimony Sb	Sb^{3+}	may react with some strong oxidizing acids	heat or physical extraction
Bismuth Bi	Bi^{3+}		
Copper Cu	Cu^{2+}	reacts slowly with air	
Tungsten W	W^{3+}	may react with some strong oxidizing acids	
Mercury Hg	Hg^{2+}		
Silver Ag	Ag^+		
Gold Au	Au^{3+}[5][6]		
Platinum Pt	Pt^{4+}		

INCREASING REACTIVITY

$E° = -2.71$ V

The Hall–Héroult Process

The Archetype for Industrial Molten-Salt Electrolysis

A Brief History of Aluminum

Wöhler, F. *Ann. Phys. (Berl.)* **1827**, *87*, 146–161.
Venetski, S. *Metallurgist* **1969**, *13*, 451–453.
Deville, H. S.-C. *De l’aluminium: ses propriétés, sa fabrication et ses applications*; Mallet-Bachelier, **1859**.
Binczewski, G. J. *JOM* **1995**, *47*, 20–25.

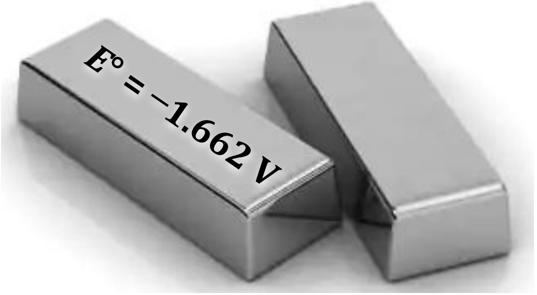
A Brief History of Aluminum

Wöhler, F. *Ann. Phys. (Berl.)* **1827**, *87*, 146–161.
Venetski, S. *Metallurgist* **1969**, *13*, 451–453.
Deville, H. S.-C. *De l'aluminium: ses propriétés, sa fabrication et ses applications*; Mallet-Bachelier, **1859**.
Binczewski, G. J. *JOM* **1995**, *47*, 20–25.

A Brief History of Aluminum

1827

Hans Christian Ørsted & Friedrich Wöhler produce pure aluminum by using potassium metal to smelt anhydrous $AlCl_3$



Wöhler, F. *Ann. Phys. (Berl.)* **1827**, *87*, 146–161.
Venetski, S. *Metallurgist* **1969**, *13*, 451–453.
Deville, H. S.-C. *De l'aluminium: ses propriétés, sa fabrication et ses applications*; Mallet-Bachelier, **1859**.
Binczewski, G. J. *JOM* **1995**, *47*, 20–25.

A Brief History of Aluminum

1827

Hans Christian Ørsted & Friedrich Wöhler produce pure aluminum by using potassium metal to smelt anhydrous $AlCl_3$

Wöhler, F. *Ann. Phys. (Berl.)* **1827**, *87*, 146–161.
Venetski, S. *Metallurgist* **1969**, *13*, 451–453.
Deville, H. S.-C. *De l'aluminium: ses propriétés, sa fabrication et ses applications*; Mallet-Bachelier, **1859**.
Binczewski, G. J. *JOM* **1995**, *47*, 20–25.

A Brief History of Aluminum

1827

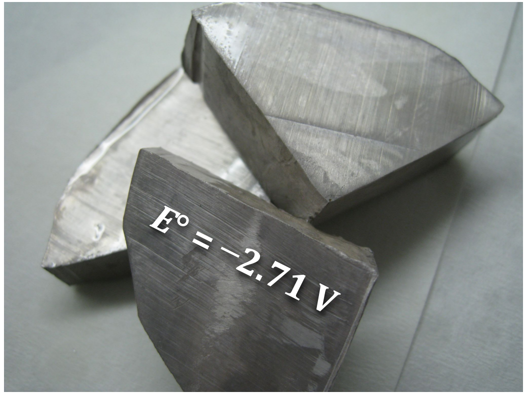
Hans Christian Ørsted & Friedrich Wöhler produce pure aluminum by using potassium metal to smelt anhydrous $AlCl_3$

Wöhler, F. *Ann. Phys. (Berl.)* **1827**, *87*, 146–161.
Venetski, S. *Metallurgist* **1969**, *13*, 451–453.
Deville, H. S.-C. *De l'aluminium: ses propriétés, sa fabrication et ses applications*; Mallet-Bachelier, **1859**.
Binczewski, G. J. *JOM* **1995**, *47*, 20–25.

A Brief History of Aluminum

1827 1859

Étienne Henry Sainte-Claire Deville replaces potassium metal with cheaper sodium



Wöhler, F. *Ann. Phys. (Berl.)* **1827**, *87*, 146–161.
Venetski, S. *Metallurgist* **1969**, *13*, 451–453.
Deville, H. S.-C. *De l'aluminium: ses propriétés, sa fabrication et ses applications*; Mallet-Bachelier, **1859**.
Binczewski, G. J. *JOM* **1995**, *47*, 20–25.

A Brief History of Aluminum

1827 — 1859 — 1884

The cap on the Washington Monument is cast out of solid aluminum

Wöhler, F. *Ann. Phys. (Berl.)* **1827**, *87*, 146–161.
Venetski, S. *Metallurgist* **1969**, *13*, 451–453.
Deville, H. S.-C. *De l'aluminium: ses propriétés, sa fabrication et ses applications*; Mallet-Bachelier, **1859**.
Binczewski, G. J. *JOM* **1995**, *47*, 20–25.

A Brief History of Aluminum

1827 1859 1884

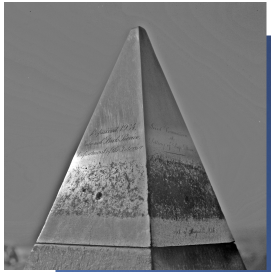
The cap on the Washington Monument is cast out of solid aluminum

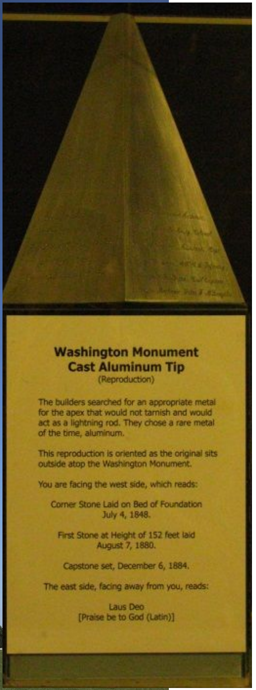
Wöhler, F. *Ann. Phys. (Berl.)* **1827**, *87*, 146–161.
Venetski, S. *Metallurgist* **1969**, *13*, 451–453.
Deville, H. S.-C. *De l'aluminium: ses propriétés, sa fabrication et ses applications*; Mallet-Bachelier, **1859**.
Binczewski, G. J. *JOM* **1995**, *47*, 20–25.

A Brief History of Aluminum

1827 **1859** **1884**

The cap on the Washington Monument is cast out of solid aluminum



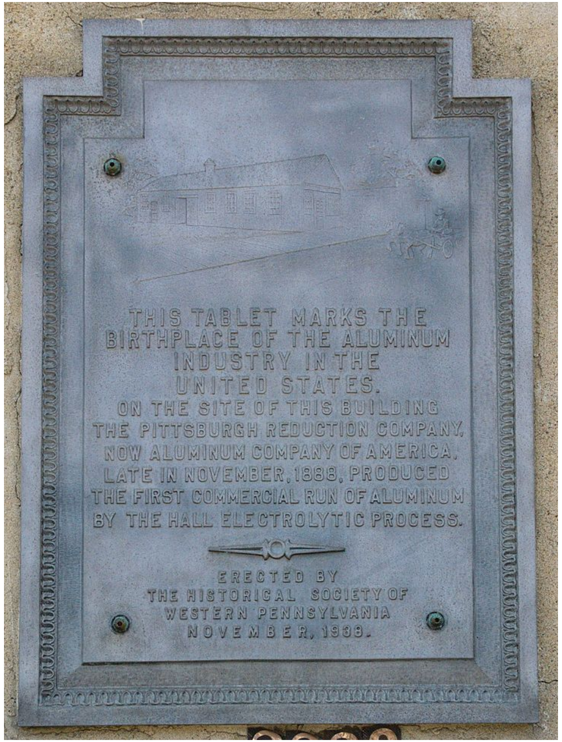


Wöhler, F. *Ann. Phys. (Berl.)* **1827**, *87*, 146–161.
Venetski, S. *Metallurgist* **1969**, *13*, 451–453.
Deville, H. S.-C. *De l'aluminium: ses propriétés, sa fabrication et ses applications*; Mallet-Bachelier, **1859**.
Binczewski, G. J. *JOM* **1995**, *47*, 20–25.

A Brief History of Aluminum

1827 | 1859 | 1884 | 1888

Charles Martin Hall and Paul L. T. Héroult independently discover the electrolytic process for aluminum production



Wöhler, F. *Ann. Phys. (Berl.)* **1827**, *87*, 146–161.
Venetski, S. *Metallurgist* **1969**, *13*, 451–453.
Deville, H. S.-C. *De l'aluminium: ses propriétés, sa fabrication et ses applications*; Mallet-Bachelier, **1859**.
Binczewski, G. J. *JOM* **1995**, *47*, 20–25.

Okay but first I need to tell you about **The Bayer Process**

- Bauxite: primary ore of aluminum
  - 30–60% $Al_2O_3 \cdot x\,H_2O$
  - Remainder: SiO_2, TiO_2, Fe_xO_y

Okay but first I need to tell you about **The Bayer Process**

- Bauxite: primary ore of aluminum
  - 30–60% $Al_2O_3 \cdot x\, H_2O$
  - Remainder: SiO_2, TiO_2, Fe_xO_y
- Bayer process makes Al_2O_3

Enserink, M. *Science* **2010**, *330* (6003), 432–433.

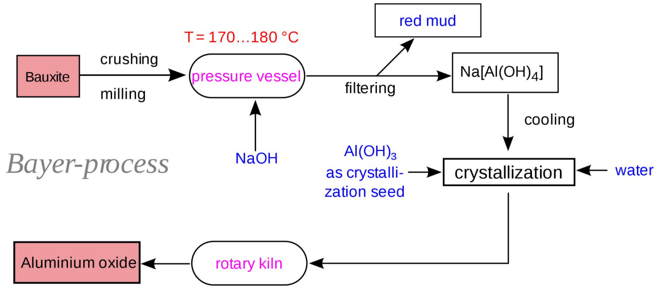
Okay but first I need to tell you about The Bayer Process

- Bauxite: primary ore of aluminum
  - 30–60% $Al_2O_3 \cdot x\, H_2O$
  - Remainder: SiO_2, TiO_2, Fe_xO_y
- Bayer process makes Al_2O_3
  - Invented 1888 by Carl Bayer

Enserink, M. *Science* **2010**, *330* (6003), 432–433.

Okay but first I need to tell you about **The Bayer Process**

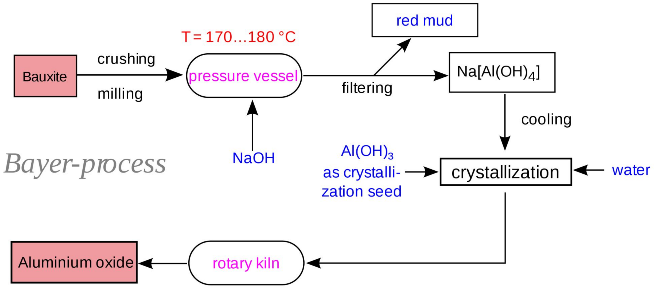
- Bauxite: primary ore of aluminum
  - 30–60% $Al_2O_3 \cdot x\, H_2O$
  - Remainder: SiO_2, TiO_2, Fe_xO_y
- Bayer process makes Al_2O_3
  - Invented 1888 by Carl Bayer



Enserink, M. *Science* **2010**, *330* (6003), 432–433.

Okay but first I need to tell you about The Bayer Process

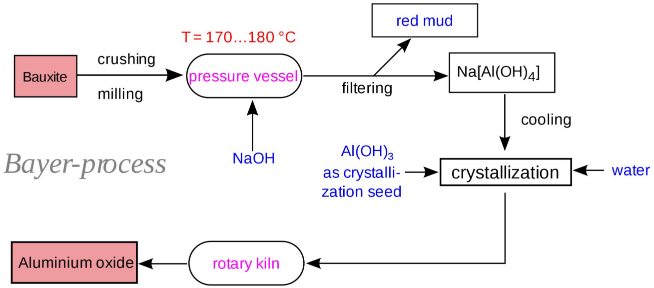
- Bauxite: primary ore of aluminum
  - 30–60% $Al_2O_3 \cdot x\, H_2O$
  - Remainder: SiO_2, TiO_2, Fe_xO_y
- Bayer process makes Al_2O_3
  - Invented 1888 by Carl Bayer
    - $Al_2O_3 + 2\ NaOH \rightarrow 2\ NaAlO_2 + H_2O$



Enserink, M. *Science* **2010**, *330* (6003), 432–433.

Okay but first I need to tell you about **The Bayer Process**

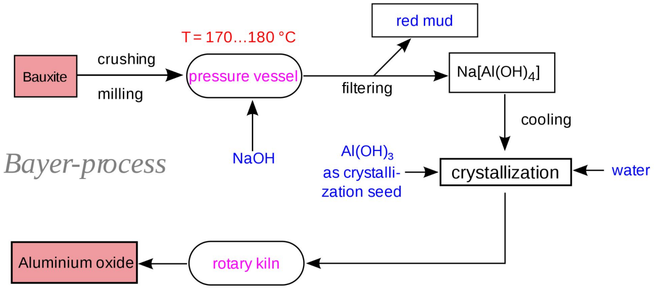
- Bauxite: primary ore of aluminum
  - 30–60% $Al_2O_3 \cdot x\,H_2O$
  - Remainder: SiO_2, TiO_2, Fe_xO_y
- Bayer process makes Al_2O_3
  - Invented 1888 by Carl Bayer
    - $Al_2O_3 + 2\ NaOH \rightarrow 2\ NaAlO_2 + H_2O$



Enserink, M. *Science* **2010**, *330* (6003), 432–433.

Okay but first I need to tell you about **The Bayer Process**

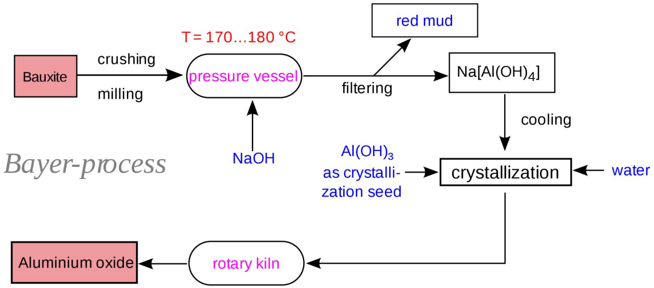
- Bauxite: primary ore of aluminum
  - 30–60% $Al_2O_3 \cdot x\, H_2O$
  - Remainder: SiO_2, TiO_2, Fe_xO_y
- Bayer process makes Al_2O_3
  - Invented 1888 by Carl Bayer
    - $Al_2O_3 + 2\ NaOH \rightarrow 2\ NaAlO_2 + H_2O$



Enserink, M. *Science* **2010**, *330* (6003), 432–433.

Okay but first I need to tell you about The Bayer Process

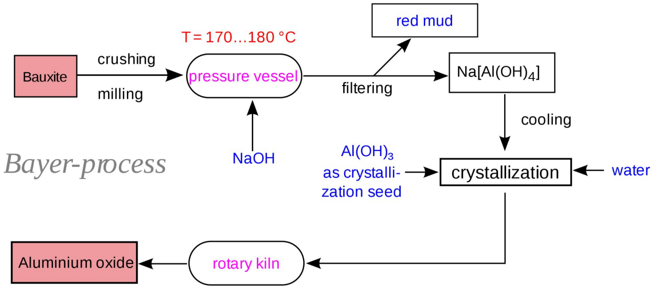
- Bauxite: primary ore of aluminum
  - 30–60% $Al_2O_3 \cdot x\, H_2O$
  - Remainder: SiO_2, TiO_2, Fe_xO_y
- Bayer process makes Al_2O_3
  - Invented 1888 by Carl Bayer
    - $Al_2O_3 + 2\ NaOH \rightarrow 2\ NaAlO_2 + H_2O$



Enserink, M. *Science* **2010**, *330* (6003), 432–433.

Okay but first I need to tell you about The Bayer Process

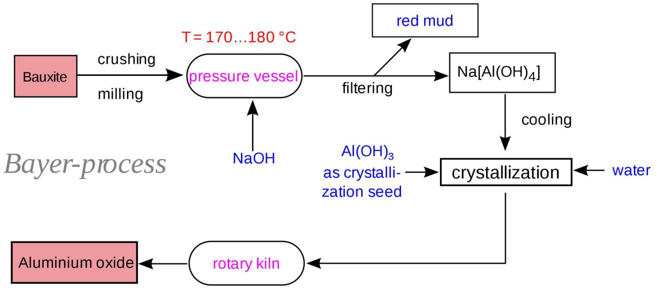
- Bauxite: primary ore of aluminum
  - 30–60% $Al_2O_3 \cdot x\ H_2O$
  - Remainder: SiO_2, TiO_2, Fe_xO_y
- Bayer process makes Al_2O_3
  - Invented 1888 by Carl Bayer
    - $Al_2O_3 + 2\ NaOH \rightarrow 2\ NaAlO_2 + H_2O$
    - $2\ H_2O + NaAlO_2 \rightarrow Al(OH)_3 + NaOH$



Enserink, M. *Science* **2010**, *330* (6003), 432–433.

Okay but first I need to tell you about The Bayer Process

- Bauxite: primary ore of aluminum
  - 30–60% $Al_2O_3 \cdot x\, H_2O$
  - Remainder: SiO_2, TiO_2, Fe_xO_y
- Bayer process makes Al_2O_3
  - Invented 1888 by Carl Bayer
    - $Al_2O_3 + 2\ NaOH \rightarrow 2\ NaAlO_2 + H_2O$
    - $2\ H_2O + NaAlO_2 \rightarrow Al(OH)_3 + NaOH$
    - $2\ Al(OH)_3 \rightarrow Al_2O_3 + 3\ H_2O$



Enserink, M. *Science* **2010**, *330* (6003), 432–433.

Finally, the Hall–Héroult Process

Finally, the Hall–Héroult Process

$$Al_2O_3 + 6\,e^- \rightarrow 2\,Al + 3\,O^{2-}$$

Finally, the Hall–Héroult Process

$$\overset{+3}{Al}_2O_3 + 6\,e^- \rightarrow 2\,\overset{0}{Al} + 3\,O^{2-}$$

Finally, the Hall–Héroult Process

reduced by 3 e⁻ / atom

$$\overset{+3}{Al}_2O_3 + 6\,e^- \rightarrow 2\,\overset{0}{Al} + 3\,O^{2-}$$

Finally, the Hall–Héroult Process

reduced by 3 e^- / atom

$$\overset{+3}{Al}_2O_3 + 6\,e^- \rightarrow 2\,\overset{0}{Al} + 3\,O^{2-}$$

$$3\,C + 3\,O^{2-} \rightarrow 3\,CO + 6\,e^-$$

Finally, the Hall–Héroult Process

reduced by 3 e^- / atom

$$\overset{+3}{\mathrm{Al}}_2\mathrm{O}_3 + 6\,e^- \longrightarrow 2\,\overset{0}{\mathrm{Al}} + 3\,\mathrm{O}^{2-}$$

$$3\,\underset{0}{\mathrm{C}} + 3\,\mathrm{O}^{2-} \longrightarrow 3\,\underset{+2}{\mathrm{C}}\mathrm{O} + 6\,e^-$$

Finally, the Hall–Héroult Process

reduced by 3 e⁻ / atom

$$\overset{+3}{Al_2O_3} + 6\,e^- \rightarrow 2\,\overset{0}{Al} + 3\,O^{2-}$$

$$3\,\underset{0}{C} + 3\,O^{2-} \rightarrow 3\,\underset{+2}{CO} + 6\,e^-$$

oxidized by 2 e⁻ / atom

Finally, the Hall–Héroult Process

$$\overbrace{\overset{+3}{Al}_2O_3 + 3\,\underset{0}{C} \rightarrow 2\,\overset{0}{Al}}^{\text{reduced by 3 e}^- \text{ / atom}} + 3\,\underset{+2}{C}O$$

reduced by 3 e⁻ / atom: Al +3 → 0

oxidized by 2 e⁻ / atom: C 0 → +2

Finally, the Hall–Héroult Process

reduced by 3 e⁻ / atom

$$\overset{+3}{\mathrm{Al}}_2\mathrm{O}_3 + 3\,\underset{0}{\mathrm{C}} \rightarrow 2\,\overset{0}{\mathrm{Al}} + 3\,\underset{+2}{\mathrm{C}}\mathrm{O}$$

oxidized by 2 e⁻ / atom

Temperature:	940–980 °C
Voltage:	~4.9 V
Current:	~5 A/cm^2

Hall–Héroult Electrolyte

Alumina (Al_2O_3) melting point: **2072 °C**

Wendt, H.; Vogt, H.; Kreysa, G.; M. Kolb, D.; E. Engelmann, G.; Ziegler, J. C.; Goldacker, H.; Jüttner, K.; Galla, U.; Schmieder, H.; Steckhan, E. Electrochemistry. In *Ullmann's Encyclopedia of Industrial Chemistry*; John Wiley & Sons, Ltd, 2008. https://doi.org/10.1002/14356007.a09_183.pub2.

Hall–Héroult Electrolyte

Alumina (Al_2O_3) melting point: **2072 °C**

Cryolite (Na_3AlF_6) melting point: **1009 °C**

Wendt, H.; Vogt, H.; Kreysa, G.; M. Kolb, D.; E. Engelmann, G.; Ziegler, J. C.; Goldacker, H.; Jüttner, K.; Galla, U.; Schmieder, H.; Steckhan, E. Electrochemistry. In *Ullmann's Encyclopedia of Industrial Chemistry*; John Wiley & Sons, Ltd, 2008. https://doi.org/10.1002/14356007.a09_183.pub2.

Hall–Héroult Electrolyte

Alumina (Al_2O_3) melting point: **2072 °C**

Cryolite (Na_3AlF_6) melting point: **1009 °C**

Wendt, H.; Vogt, H.; Kreysa, G.; M. Kolb, D.; E. Engelmann, G.; Ziegler, J. C.; Goldacker, H.; Jüttner, K.; Galla, U.; Schmieder, H.; Steckhan, E. Electrochemistry. In *Ullmann's Encyclopedia of Industrial Chemistry*; John Wiley & Sons, Ltd, 2008. https://doi.org/10.1002/14356007.a09_183.pub2.

Hall–Héroult Electrolyte

Alumina (Al_2O_3) melting point: **2072 °C**

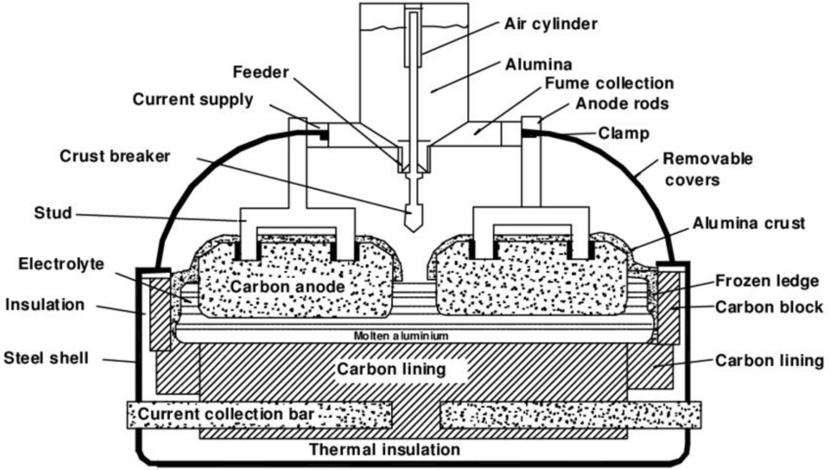
Cryolite (Na_3AlF_6) melting point: **1009 °C**

10% Al_2O_3 : Na_3AlF_6

eutectic MP: **960 °C**

Wendt, H.; Vogt, H.; Kreysa, G.; M. Kolb, D.; E. Engelmann, G.; Ziegler, J. C.; Goldacker, H.; Jüttner, K.; Galla, U.; Schmieder, H.; Steckhan, E. Electrochemistry. In *Ullmann's Encyclopedia of Industrial Chemistry*; John Wiley & Sons, Ltd, 2008. https://doi.org/10.1002/14356007.a09_183.pub2.

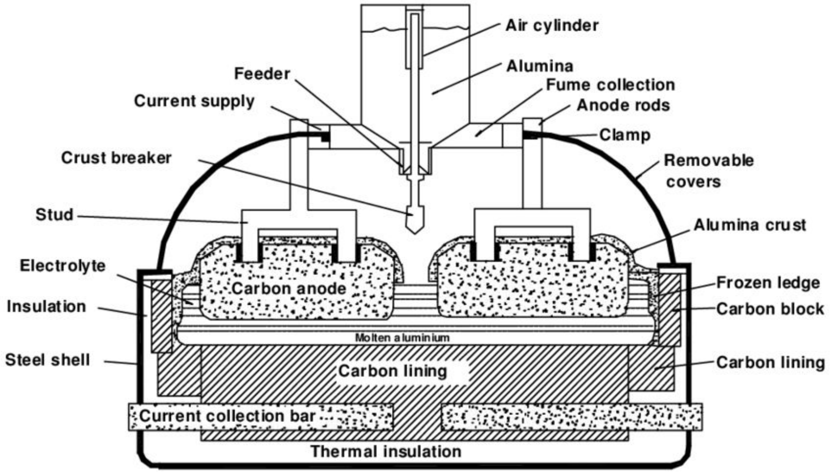
Hall–Héroult Reactor Layout



Wendt, H.; Vogt, H.; Kreysa, G.; M. Kolb, D.; E. Engelmann, G.; Ziegler, J. C.; Goldacker, H.; Jüttner, K.; Galla, U.; Schmieder, H.; Steckhan, E. Electrochemistry. In *Ullmann's Encyclopedia of Industrial Chemistry*; John Wiley & Sons, Ltd, 2008. https://doi.org/10.1002/14356007.a09_183.pub2.

Hall–Héroult Reactor Layout

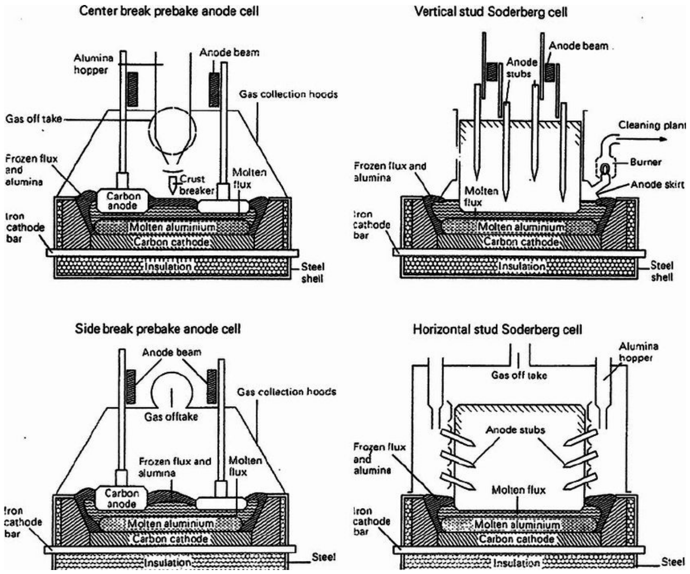
"The cell is composed of an outer carbon or graphite lining and a row of adjustable prebaked carbon anodes. At the bottom of the pot there is the cathode, a pool of liquid aluminum, which is emptied periodically by suction and which is covered by the molten electrolyte into which are immersed the gas-evolving anodes. The melt is covered by a crust of solid electrolyte and a supply of fresh, loose Al_2O_3. Periodically crushing this crust serves to replenish the Al_2O_3 content of the bath."



Wendt, H.; Vogt, H.; Kreysa, G.; M. Kolb, D.; E. Engelmann, G.; Ziegler, J. C.; Goldacker, H.; Jüttner, K.; Galla, U.; Schmieder, H.; Steckhan, E. Electrochemistry. In *Ullmann's Encyclopedia of Industrial Chemistry*; John Wiley & Sons, Ltd, 2008. https://doi.org/10.1002/14356007.a09_183.pub2.

Electrode Properties and Geometry

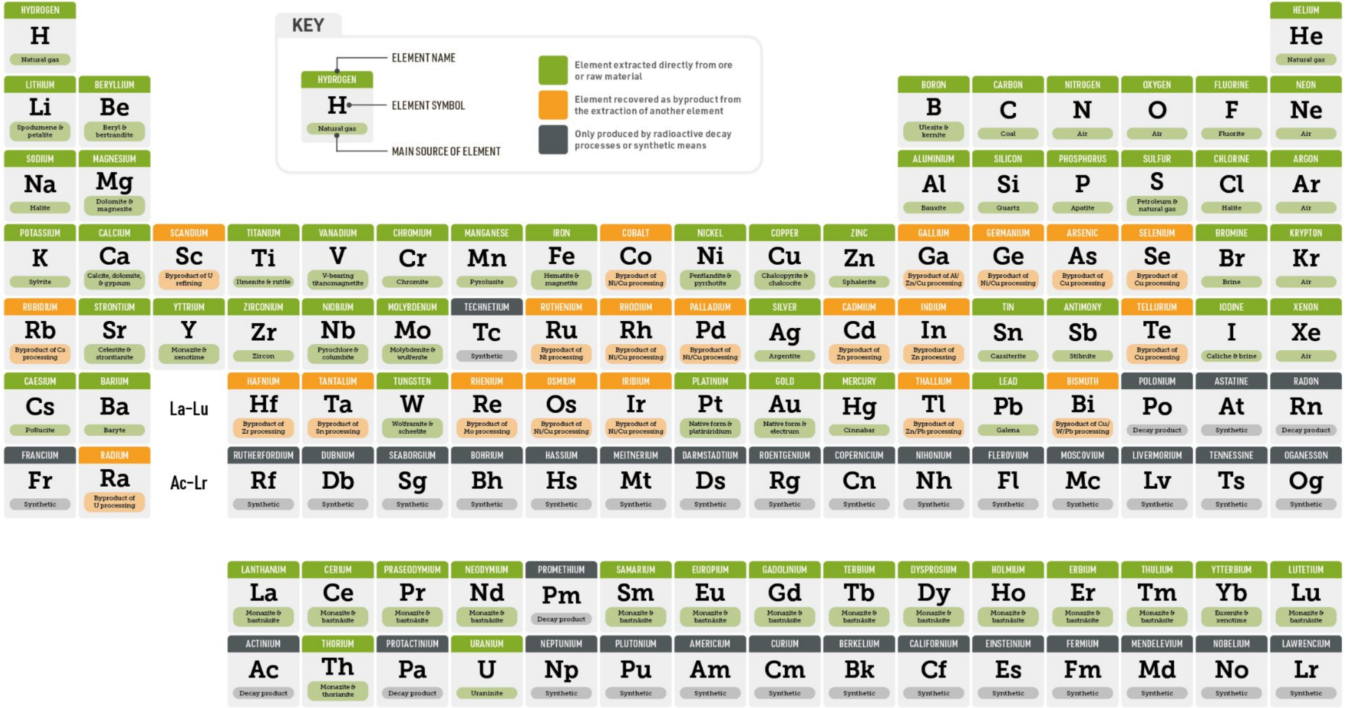
- Anode/Cathode: carbon
  - “Prebaked” or “self-baking” (Söderberg)
  - Up to 150 cm diameter
  - Interelectrode distance: 8 cm
- Melt container also made of carbon
- “Sacrificial anode” must be continuously replaced to account for oxidation
  - Prebaked: 0.47 kg/kg Al
  - Söderberg: 0.55 kg/kg Al
  - Theoretical limit: 0.33 kg/kg Al)
- Current inhomogeneities (“anode effect”) may create CF_x species



Vohler, O.; Nutsch, G.; Collin, G.; von Sturm, F.; Wege, E.; Frohs, W.; Henning, K.-D.; von Kienle, H.; Voll, M.; Kleinschmit, P.; Vostrowsky, O.; Hirsch, A. Carbon. In *Ullmann’s Encyclopedia of Industrial Chemistry*; John Wiley & Sons, Ltd, 2010. https://doi.org/10.1002/14356007.a05_095.

11

THE PERIODIC TABLE OF ELEMENT PRODUCTION SOURCES

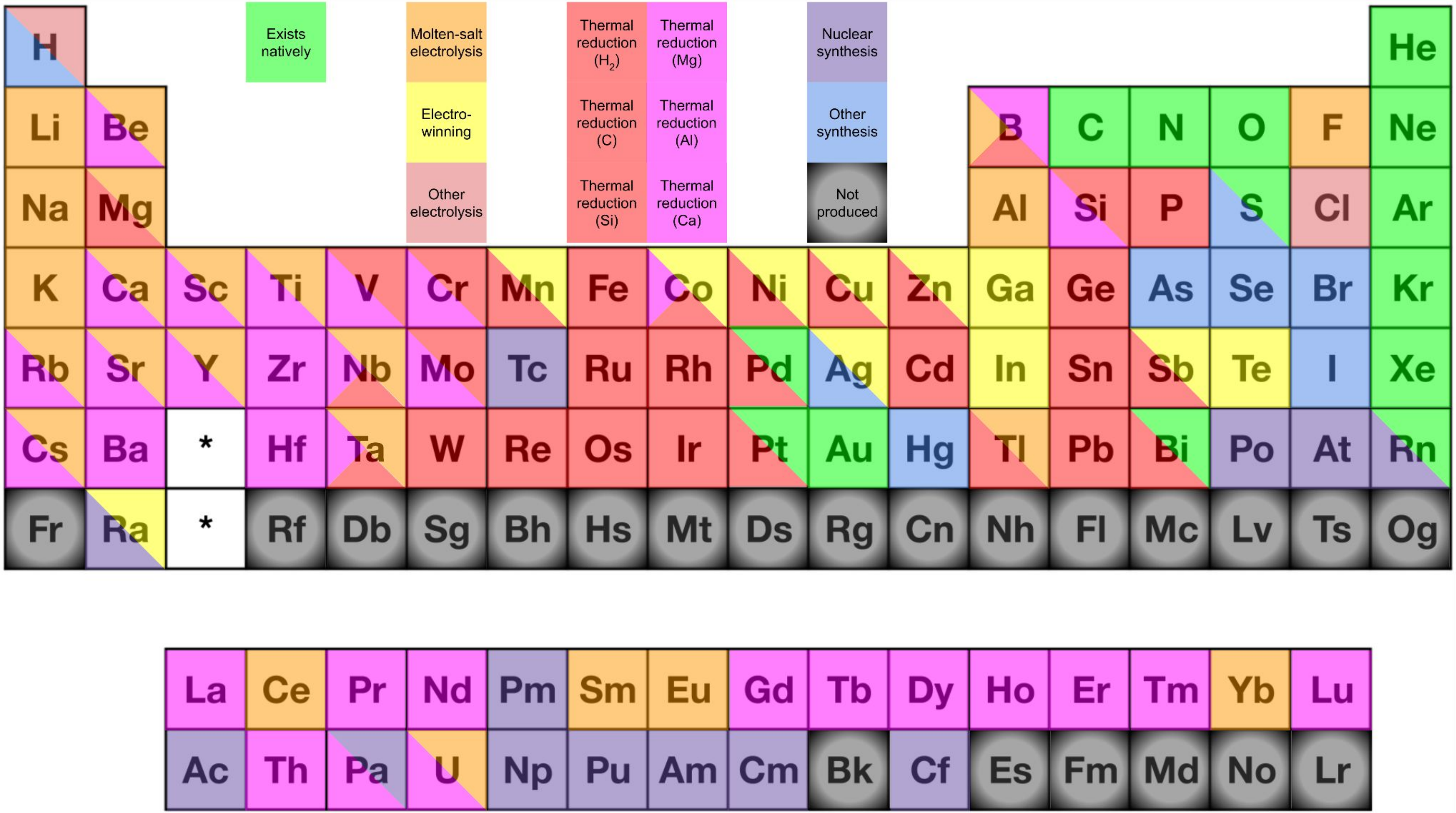


Source data: Minerals Education Coalition, https://mineralseducationcoalition.org/mining-minerals-information/periodic-table-of-the-elements/

#IYPT2019

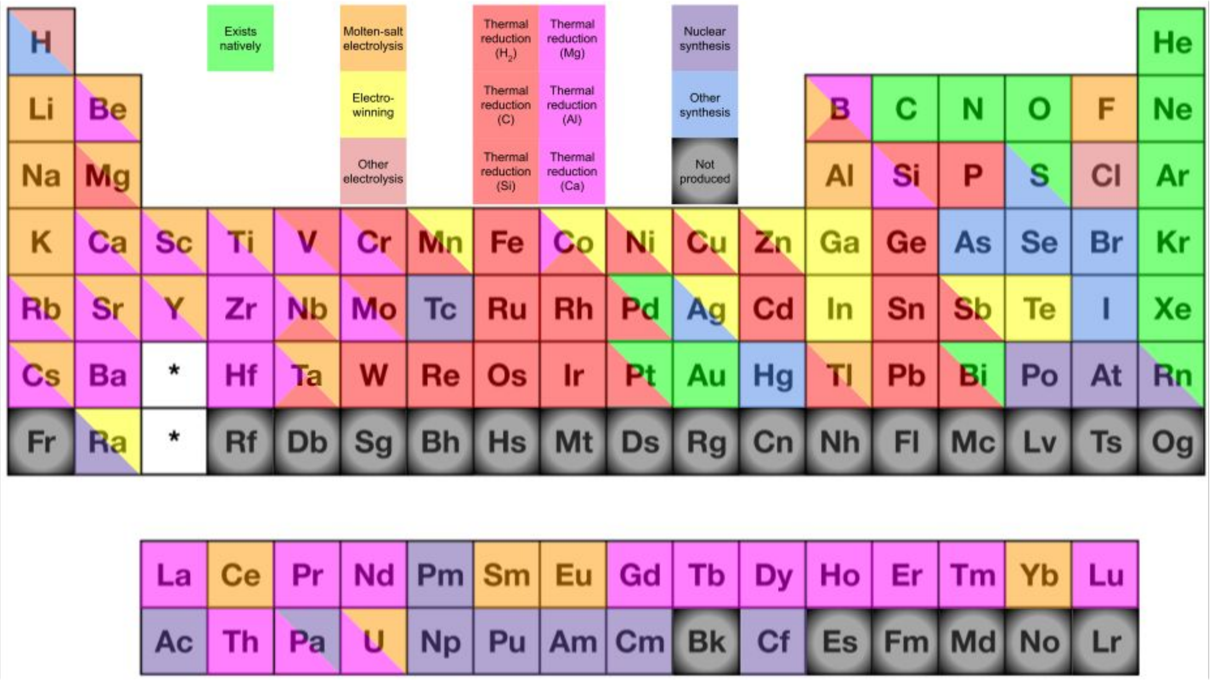
Element	Exists Natively	Electrolysis (molten-salt)	Electrowinning	Electrolysis (other)	Reduction (hydrogen)	Reduction (carbothermic)	Reduction (aluminothermic)	Reduction (magnesium)	Reduction (silicothermic)	Reduction (calciothermic)	Nuclear Synthesis	Not Produced	other	notes	molten-salt T	molten-salt elyte
Hydrogen													methane pyrolysis, steam methane reforming			
Helium														from natural gas		
Lithium															400-460 C	Li:KCl eutectic
Beryllium														Mg reduction of BeF2 at 1300 C	400-600 C	Na:BeCl2 eutectic
Boron															800 C	KBF4 / KCl:KF
Carbon																
Nitrogen														from air		
Oxygen														from air		
Fluorine														Moissan process	70-130 C	KF • 2HF
Neon														from air		
Sodium														also carbothermal reduction of Na2CO3 and Castner process electrc	700 C	Na:CaCl2 eutectic
Magnesium														US: Dow process (electrolysis); China/Russia: Pidgeon process (car	700-800 C	MgCl2
Aluminum														Hall process	950-1000 C	Al2O3 / Na3AlF6 / CaF2
Silicon																
Phosphorus																
Sulfur													Claus process for desulfurization of H2S in natural gas			
Chlorine														chloralkali process		
Argon																
Potassium													reduction of molten KCl with metallic Na		870 C	KCl
Calcium														US: aluminothermic CaO reduction; China/Russia: Davy method (ele	780-800 C	CaCl2
Scandium															900 C	Sc2O3 / CaCl2
Titanium														Kroll process (magnesium); FFC Cambridge process (electrochemic	900-1100 C	TiO2 / CaCl2
Vanadium																
Chromium																
Manganese																
Iron																
Cobalt																
Nickel																
Copper													thermal decomposition of Cu2O			
Zinc																
Gallium														from Bayer process slag	50-75 C	gallium aluminate
Germanium																
Arsenic													thermal decomposition of arsenic oxides			
Selenium													reductive sulfatic	from Cu slag		
Bromine													ion replacement with chloride (oxidation by Cl2)			
Krypton														from air		
Rubidium															750 C	RbCl
Strontium														can be produced by electrolysis of SrCl2 / KCl	1000 C	SrCl2 / KCl
Yttrium															900 C	Y2O3 / CaCl2
Zirconium														Kroll process (like Ti/Hf)		
Niobium															900-1100 C	K2[NbOF5] / NaCl
Molybdenum																
Technetium																
Ruthenium																
Rhodium														refining is the hard part, not reduction		
Palladium													catalytic converter recycling (lol)			

Greenwood, N. N.; Earnshaw, A. Chemistry of the Elements; Elsevier, **2012**, among many other sources.



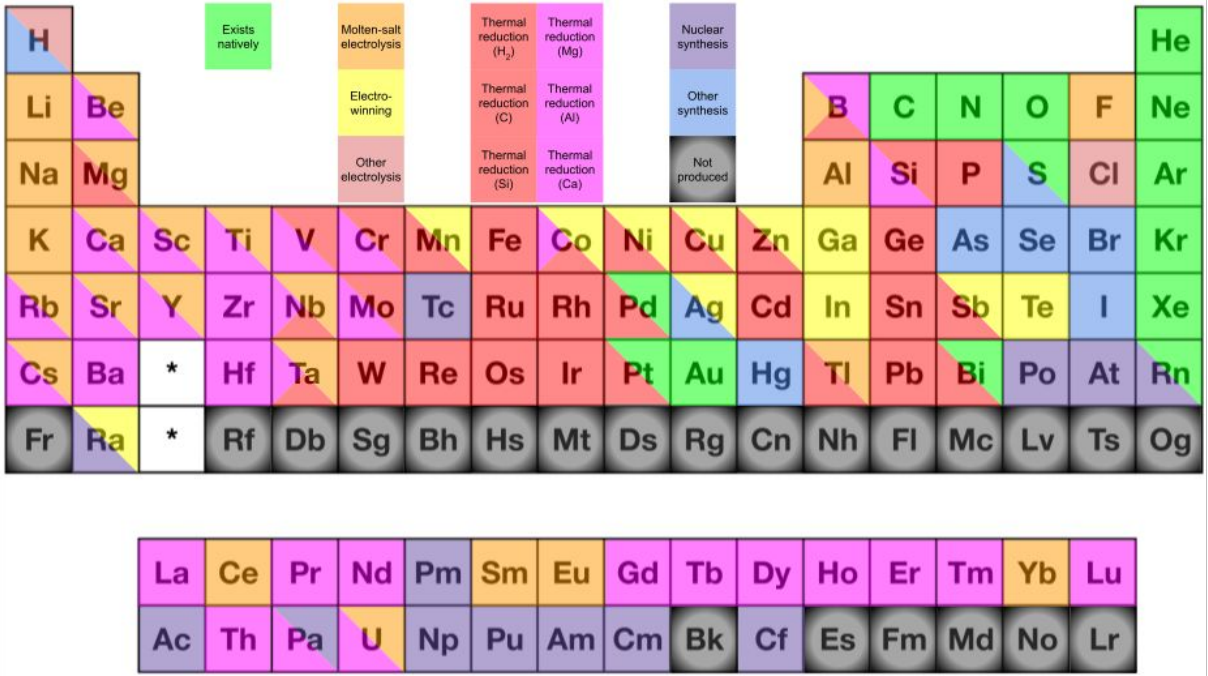
Exists natively
Molten-salt electrolysis
Electro-winning
Other electrolysis
Thermal reduction (H_2)
Thermal reduction (Mg)
Thermal reduction (C)
Thermal reduction (Al)
Thermal reduction (Si)
Thermal reduction (Ca)
Nuclear synthesis
Other synthesis
Not produced
H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba * Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra * Rf Db Sg Bh Hs Mt Ds Rg Cn Nh Fl Mc Lv Ts Og
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr

Industrial Synthesis of Pure Elements



Industrial Synthesis of Pure Elements

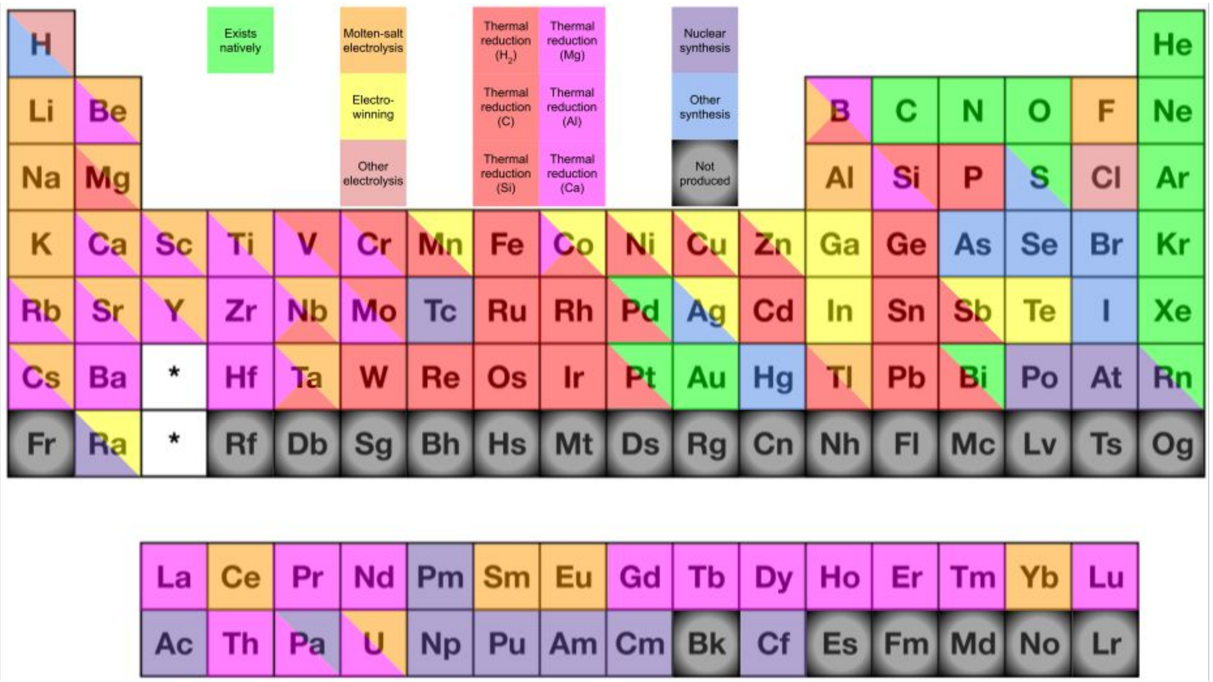
H_2 / C / Si:
produced thermochemically



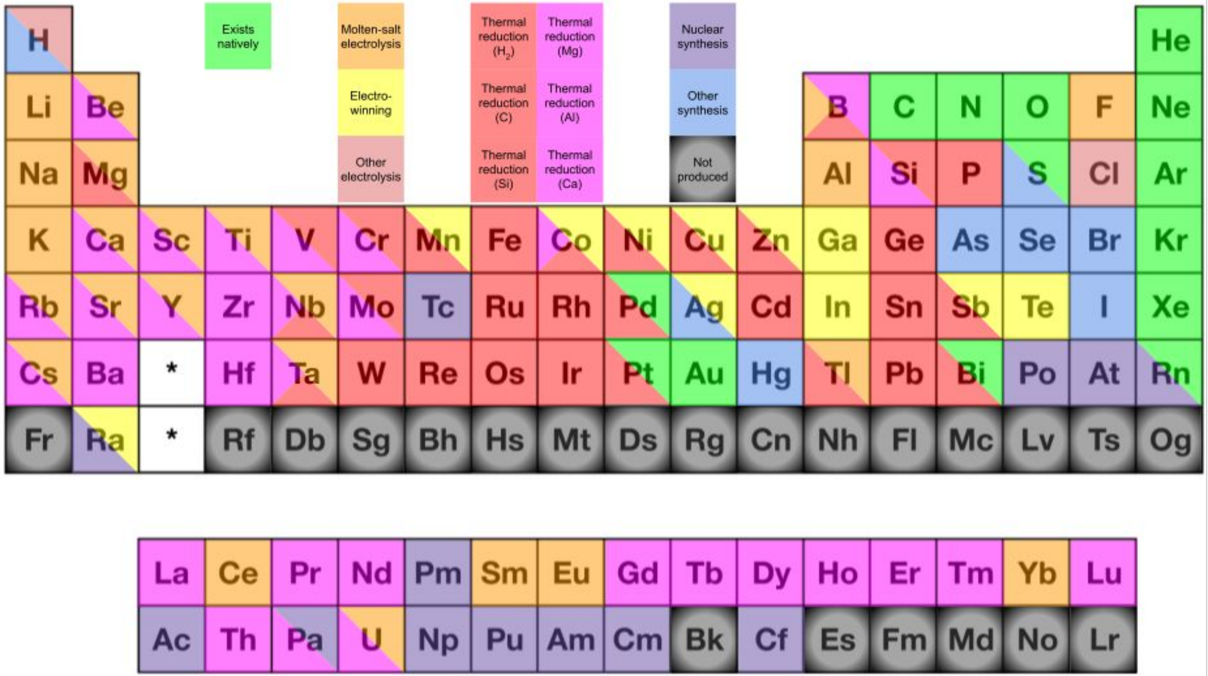
Industrial Synthesis of Pure Elements

H_2 / C / Si:
produced thermochemically

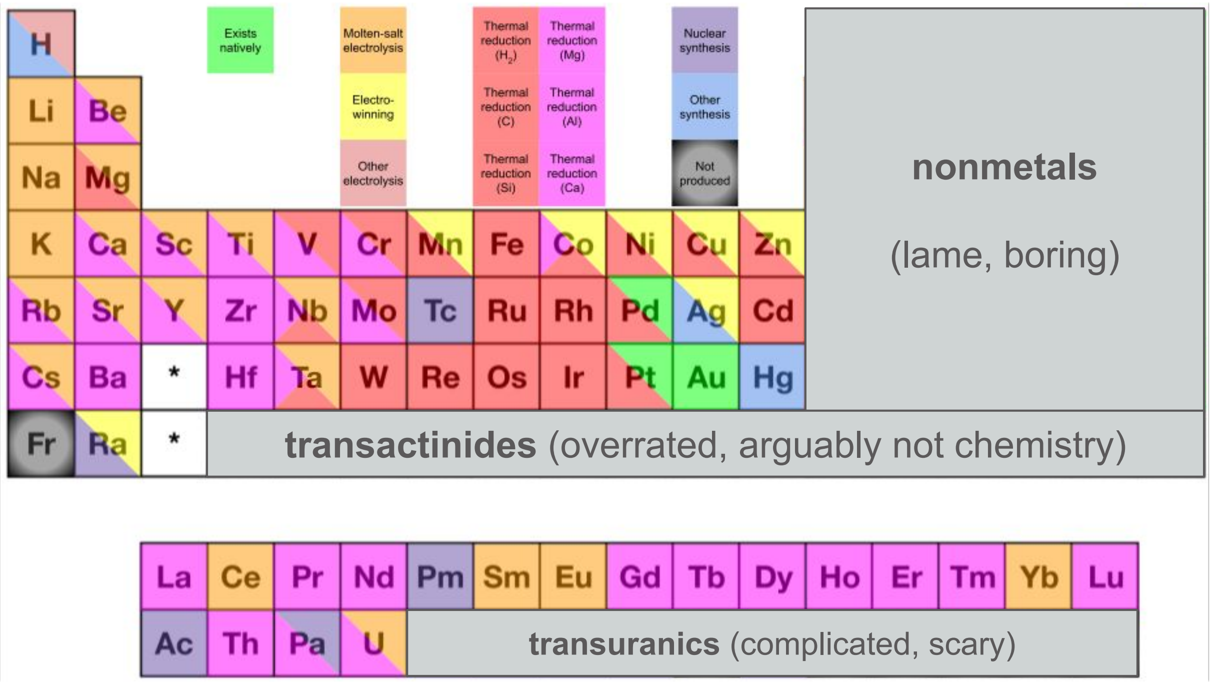
Mg / Al / Ca:
produced electrochemically



Industrial Synthesis of Pure Elements

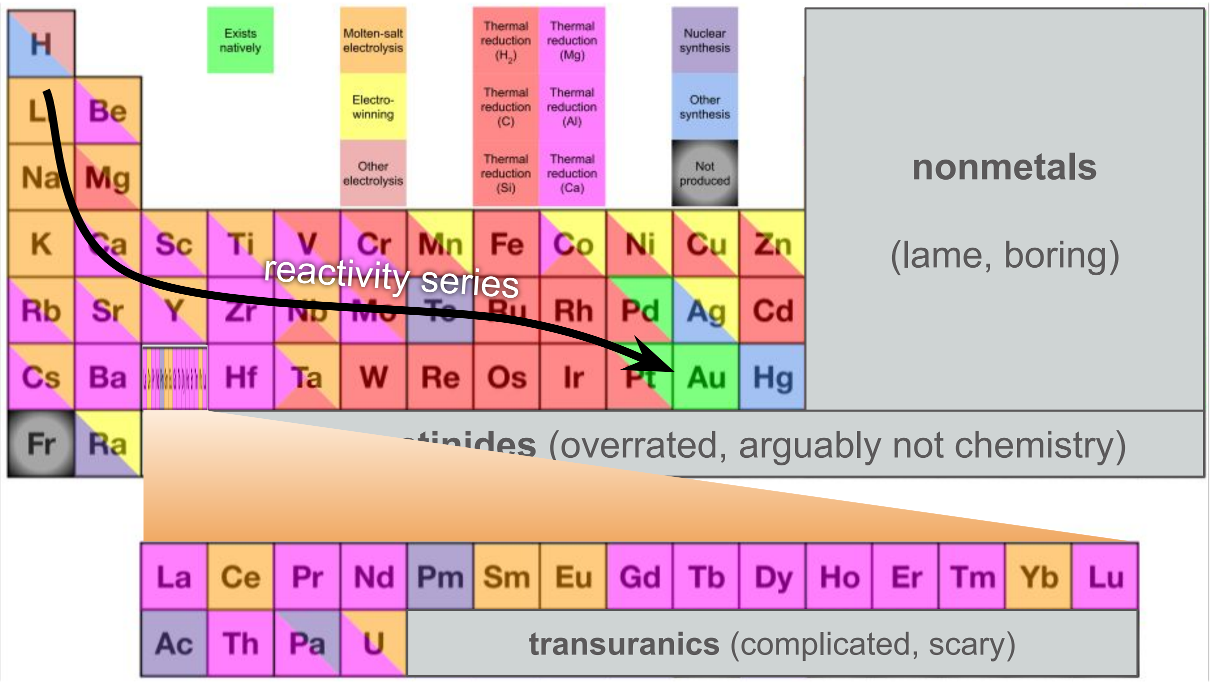


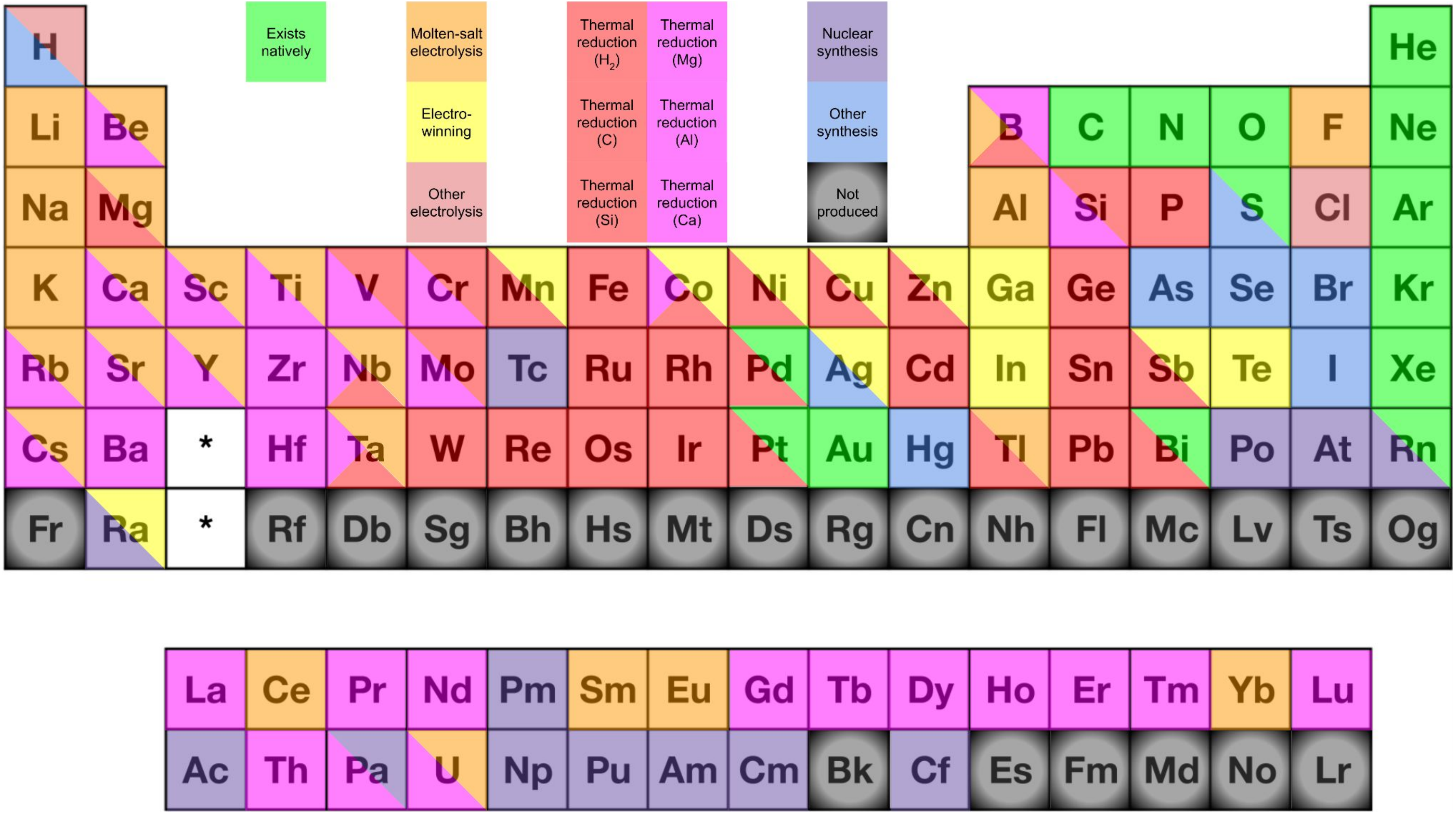
Industrial Synthesis of Pure Elements

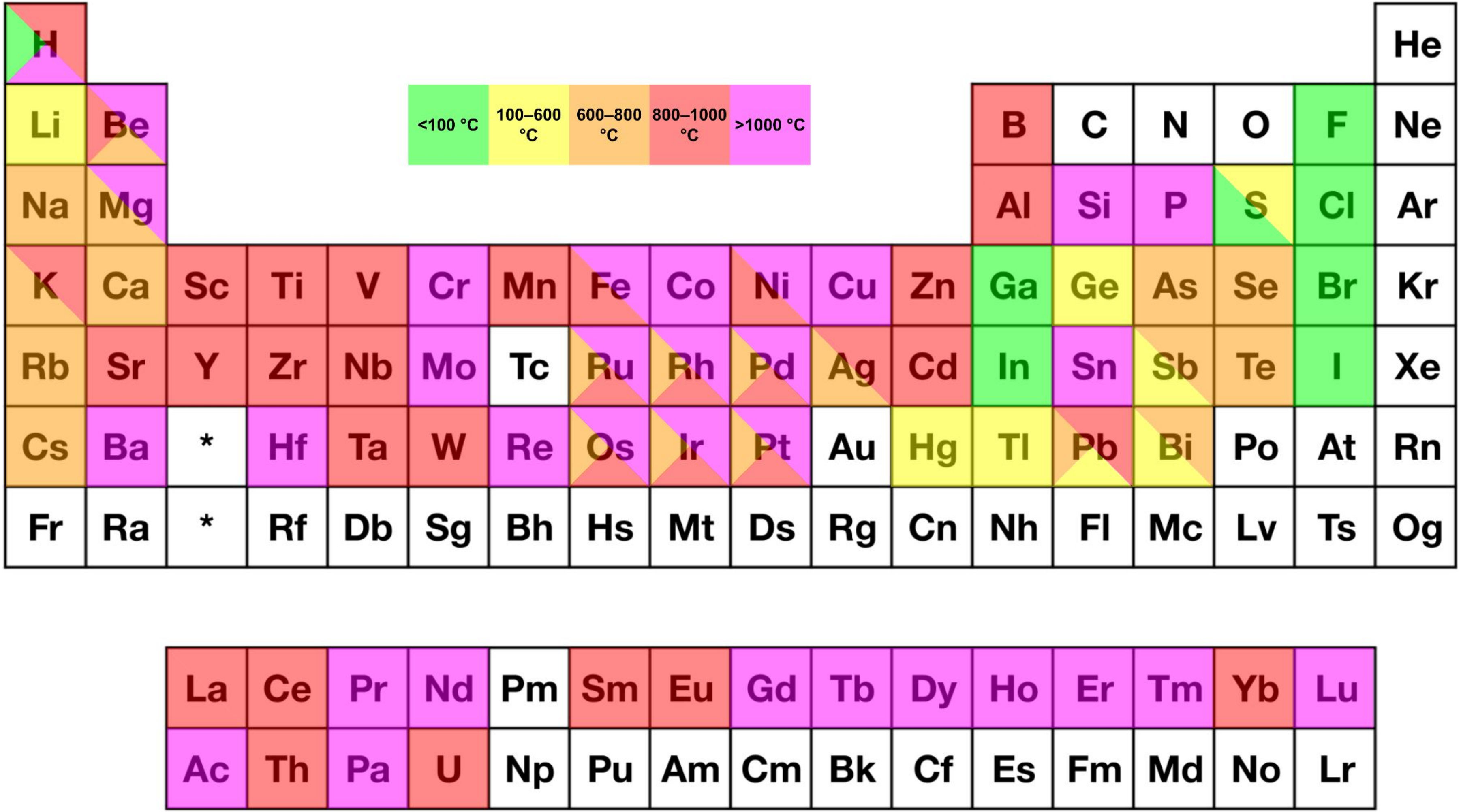


Industrial Synthesis of Pure Elements

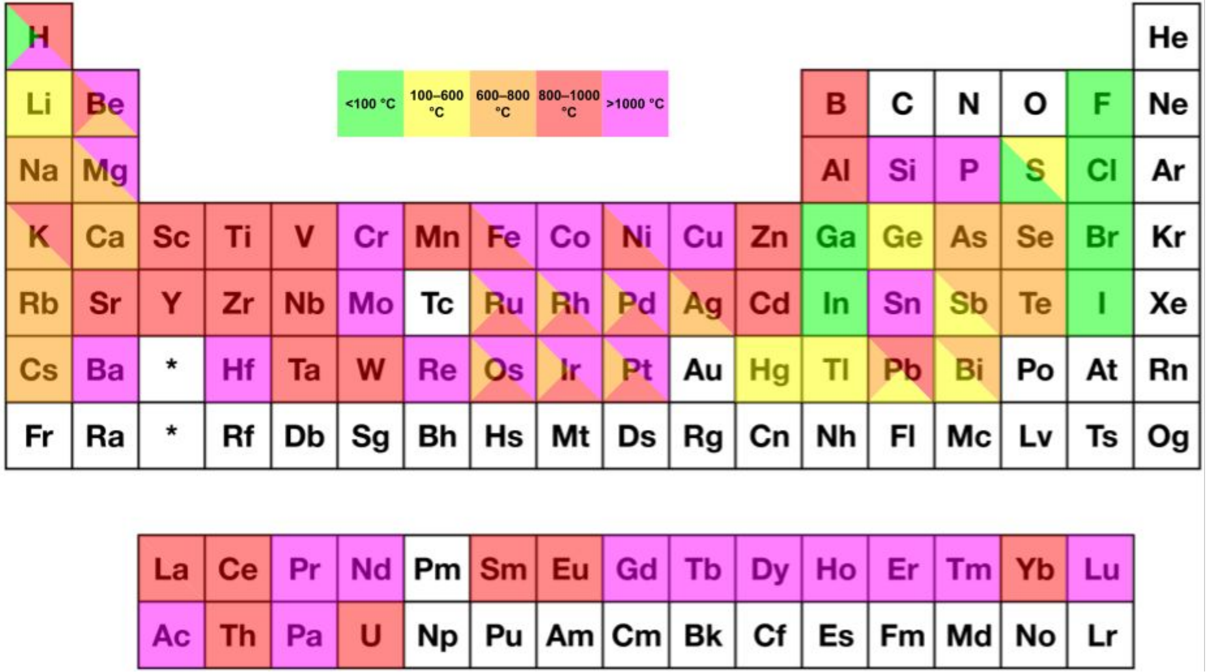
1. Molten-salt electrolysis
2. Thermochemical reduction (Mg/Ca/Al)
3. Thermochemical reduction (Si/H_2/C)
4. Electrowinning




Exists natively
Molten-salt electrolysis
Electro-winning
Other electrolysis
Thermal reduction (H_2)
Thermal reduction (Mg)
Thermal reduction (C)
Thermal reduction (Al)
Thermal reduction (Si)
Thermal reduction (Ca)
Nuclear synthesis
Other synthesis
Not produced
H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba * Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra * Rf Db Sg Bh Hs Mt Ds Rg Cn Nh Fl Mc Lv Ts Og
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr


<100 °C
100–600 °C
600–800 °C
800–1000 °C
>1000 °C
H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba * Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra * Rf Db Sg Bh Hs Mt Ds Rg Cn Nh Fl Mc Lv Ts Og
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr

What’s the Temperature, Kenneth?



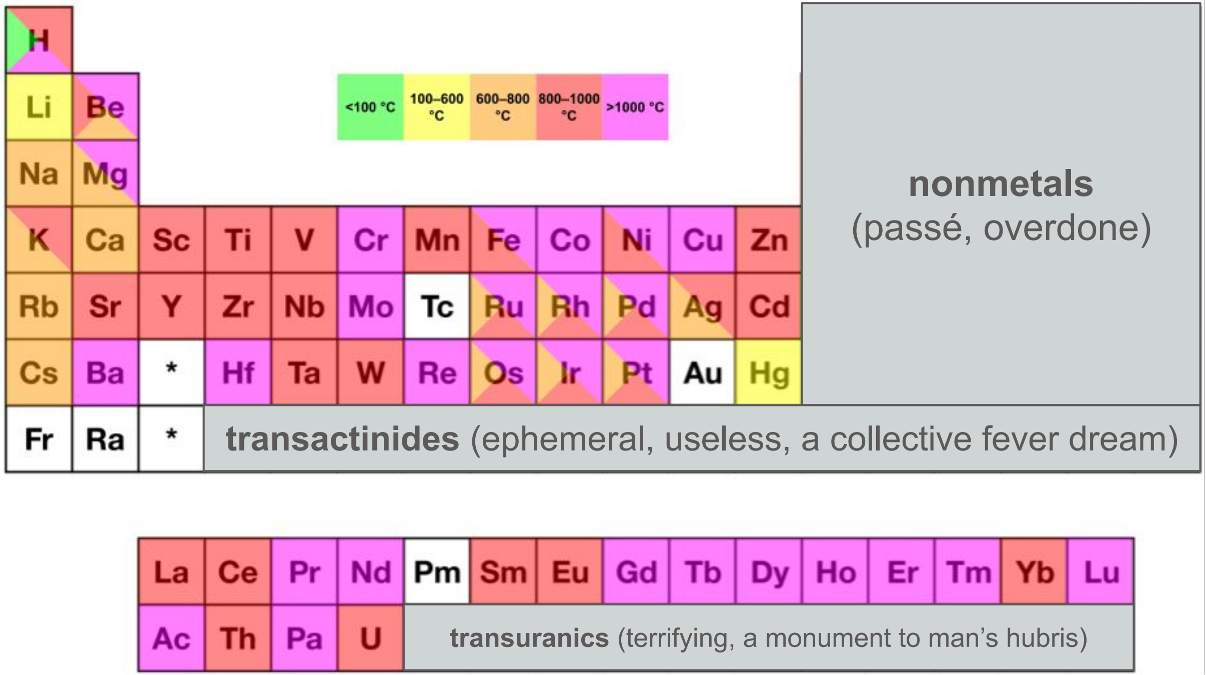
What's the Temperature, Kenneth?

<600 °C:
electrowinning, some eutectic electrolyses

600-800 °C:
most salt electrolyses

800-1000 °C:
most Mg/Ca/Al reduction

>1000 °C:
most C/H_2/Si reduction

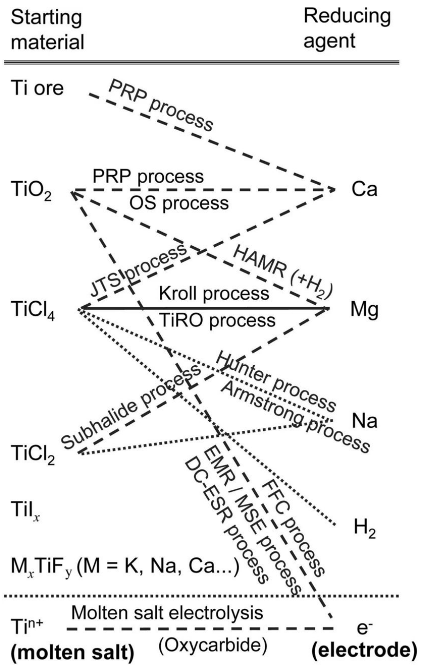


Case Study: Titanium Refining

- **Past:** reduction with Na (Hunter Process, 1950-1993)
- **Present:** reduction by Mg (Kroll Process):
  1. $TiO_2 + 2\ Cl_2 + C \rightarrow TiCl_4 + CO_2$ (T = 900 °C)
  2. $TiCl_4$ is distilled off from $AlCl_3$, $VOCl_3$, $SnCl_4$, etc.
  3. $TiCl_4 + 2\ Mg \rightarrow Ti + 2\ MgCl_2$ (T = 1100 °C)
  4. $MgCl_2$ electrolysis to Mg metal
- **Future?:** electrolysis of TiO_2 (FFC Cambridge Process)

  Electrolyte: $CaCl_2$ melt (T > 800 °C)

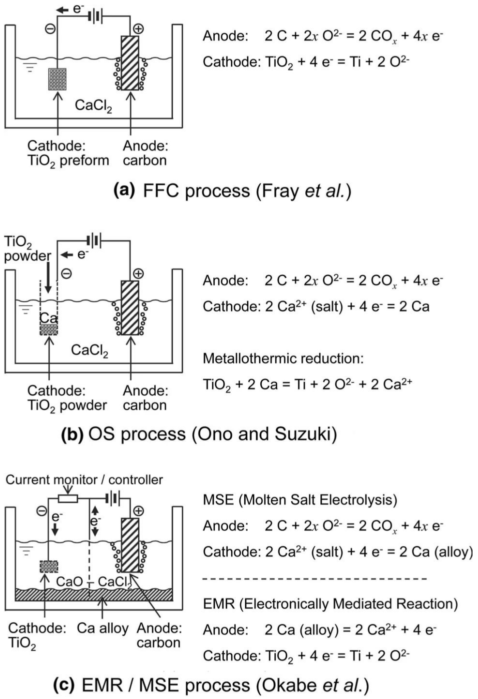
  Metalysis, Inc. (UK) developing pilot cell



Takeda, O.; Ouchi, T.; Okabe, T. H. *Metall. Mater. Trans. B* **2020**, *51*, 1315.

Case Study: Titanium refining

"The direct reduction of titanium oxide seems reasonable as a reduction process; however, an inexpensive method for the production of high-purity titanium oxide by removing iron, aluminum, silicon, etc., from titanium ores has not been developed to date. At this stage, the purity of TiO_2 obtained by upgrading is at most 96%, and a more advanced process is required, like the Bayer process in aluminum smelting (achieving 99.5% pure Al_2O_3)."



I. Mellor, G. Doughty, M. Piper, T. Ellis, K. Rao, J. Dean. *Proc. 13th World Conf. Titanium*, **2016**, pp. 145–50.

Broader Outlook for Melt Electrolysis

- Mn ($E°$ = -1.05 V) is the most reactive metal that can be electrodeposited from aqueous solution
  - Less active metals (e.g. Sn, Pb) can be produced by electrowinning
  - More active metals (e.g. Al, Ti) can only be electrolyzed from a melt
- Electrolysis requires highly purified oxide starting material
  - The Bayer process is inextricable from the Hall process because it produces very pure Al_2O_3 from crude bauxite ore
    - The Bayer process is responsible for 40-50% of the production cost of Al!
  - No equivalent to the Bayer process yet exists for most other light metals

Metal	State	E° (V)
Lithium	1+	- 3.05
Potassium	1+	- 2.93
Calcium	2+	- 2.87
Sodium	1+	- 2.71
Magnesium	2+	- 2.37
Aluminum	3+	- 1.66
Manganese	2+	- 1.18
Zinc	2+	- 0.76
Chromium	3+	- 0.74
Iron (II)	2+	- 0.44
Cadmium	2+	- 0.40
Cobalt	2+	- 0.28
Nickel	2+	- 0.25
Tin (II)	2+	- 0.14
Lead	2+	- 0.13
Hydrogen	1+	0.00
Tin (IV)	4+	0.15
Copper	2+	0.16
Iron (III)	3+	0.77
Silver	1+	0.80
Platinum	2+	1.20
Gold	1+	1.68

DECREASING ACTIVITY

Wendt, H.; Vogt, H.; Kreysa, G.; M. Kolb, D.; E. Engelmann, G.; Ziegler, J. C.; Goldacker, H.; Jüttner, K.; Galla, U.; Schmieder, H.; Steckhan, E. Electrochemistry. In *Ullmann's Encyclopedia of Industrial Chemistry*; John Wiley & Sons, Ltd, **2008**.
Haupin, W. E.; Frank, W. B. *Compr. Treatise Electrochem.* **1981**, 2, 301.

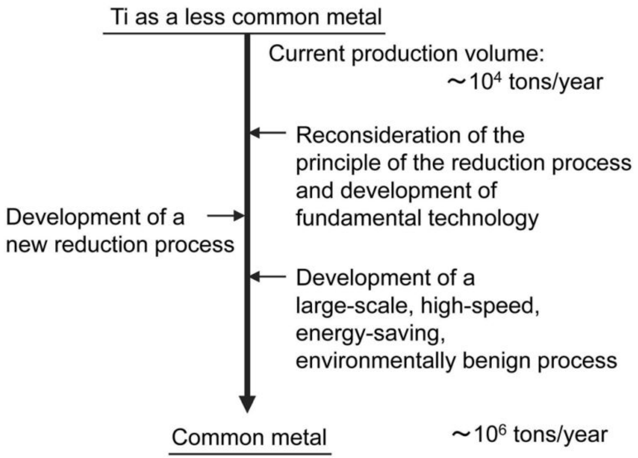
Outlook for CSP Integration

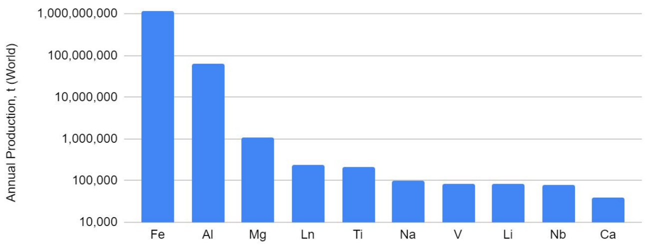
- \+ May reduce rxn temp to range accessible by Gen3 CSP
- \+ Emissions reductions likely vs. incumbent processes
- \+ Potential for retrofitting (high electricity use already there)

- − Temp demand may be 800-1000 °C or greater (perhaps beyond Gen3)
- − Demands novel preprocessing steps for ore purification
- − Inert anode R&D needed to reach true zero emissions

Suggested CSP Integration Foci

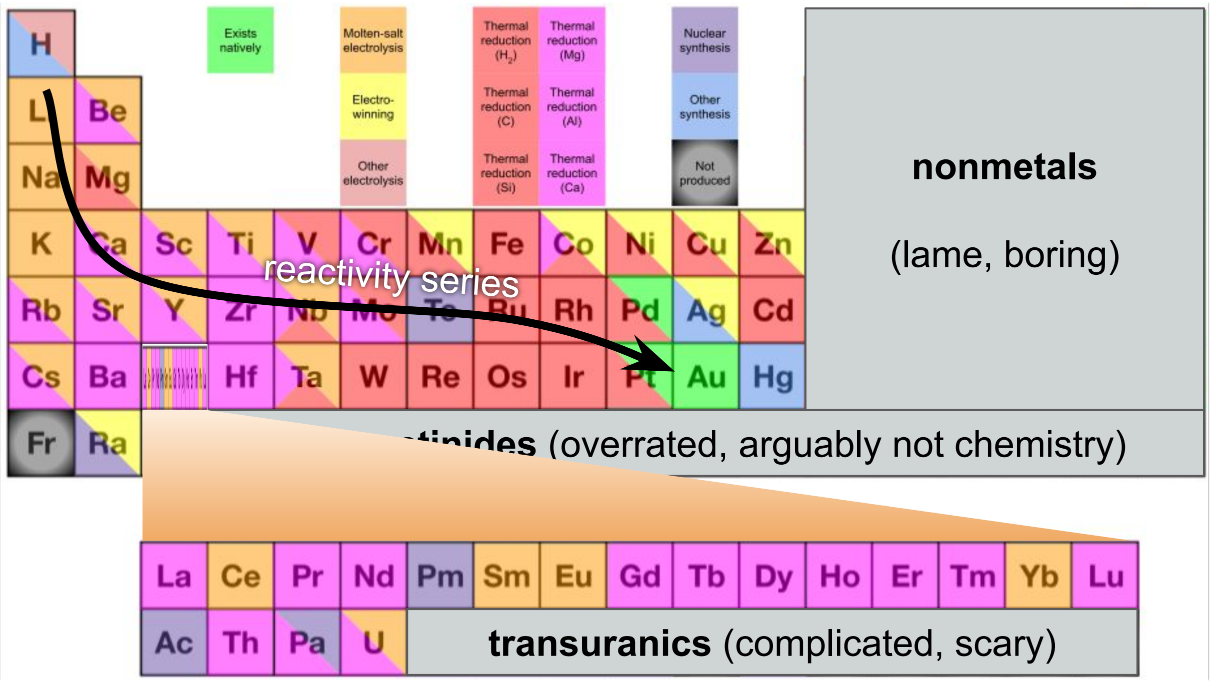
- Titanium refining
- Lanthanide separation
- Magnesium electrolysis





How are pure elements made today?

1. Molten-salt electrolysis
2. Thermochemical reduction (Mg/Ca/Al)
3. Thermochemical reduction (Si/H_2/C)
4. Electrowinning



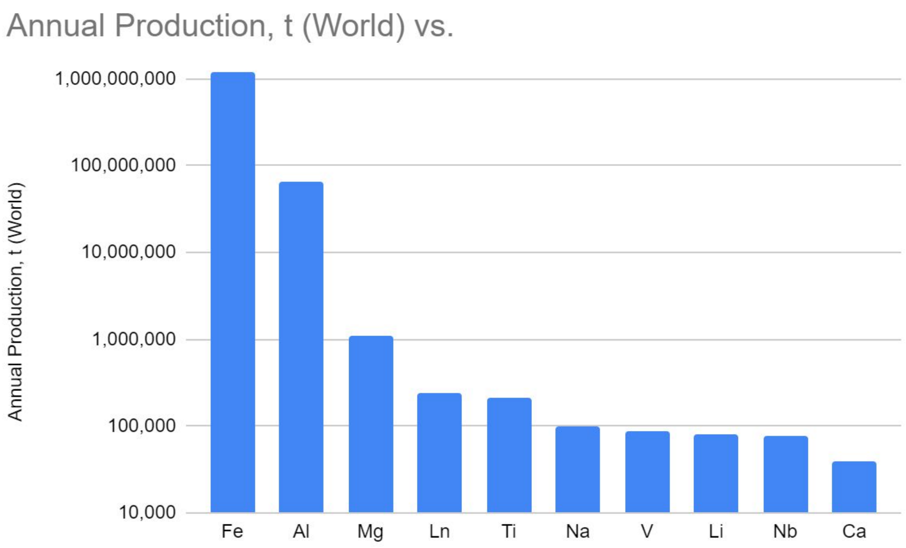
Other metals

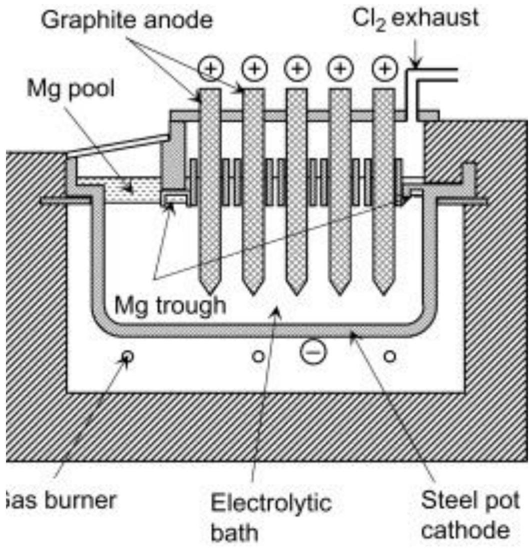
- Al:
  - 1 M
  - 65.

Mg: “”

Na: “”

Ca: “”





U.S. Geological Survey. *Mineral Commodity Summaries 2021*; U.S. Geological Survey, 2021; p 200.

Ln: “” 240 kt/yr $3.8bn