Research on Extractive Metallurgy of Magnet Materials

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NDIA

Mine-to-Magnet Workshop

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COLORADO SCHOOL OF
MINES
@150 | 1874-2024

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  KIEM Director
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CMI
Critical Materials Institute
AN ENERGY INNOVATION HUB

CR3
Center for Resource Recovery & Recycling

KIEM
Kroll Institute for Extractive Metallurgy
@50 |1974-2024

KIEM, Research Center in the Department of Mining Engineering

- Established in 1974 using funds provided by William Kroll who invented Ti/Zr process.
- Has supported for many UG/GR students who have gone on to make important contribution to the mining, minerals and metals industry.
- The objectives are to provide research expertise, well-trained engineer to industry, and research and educational opportunities to students, in the area of mineral processing, extractive metallurgy, recycling, and waste minimization.

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.

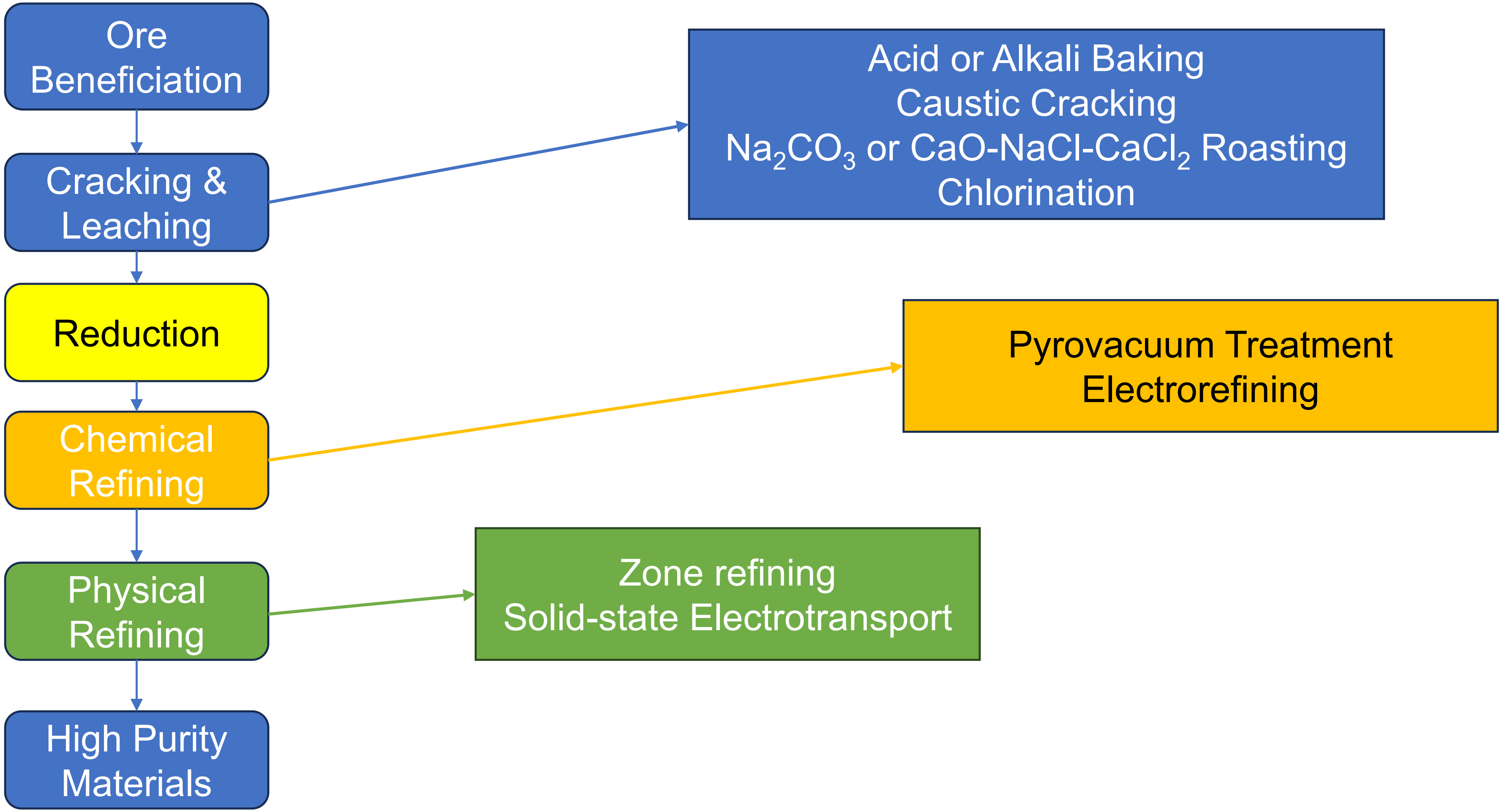
KIEM Accomplishments

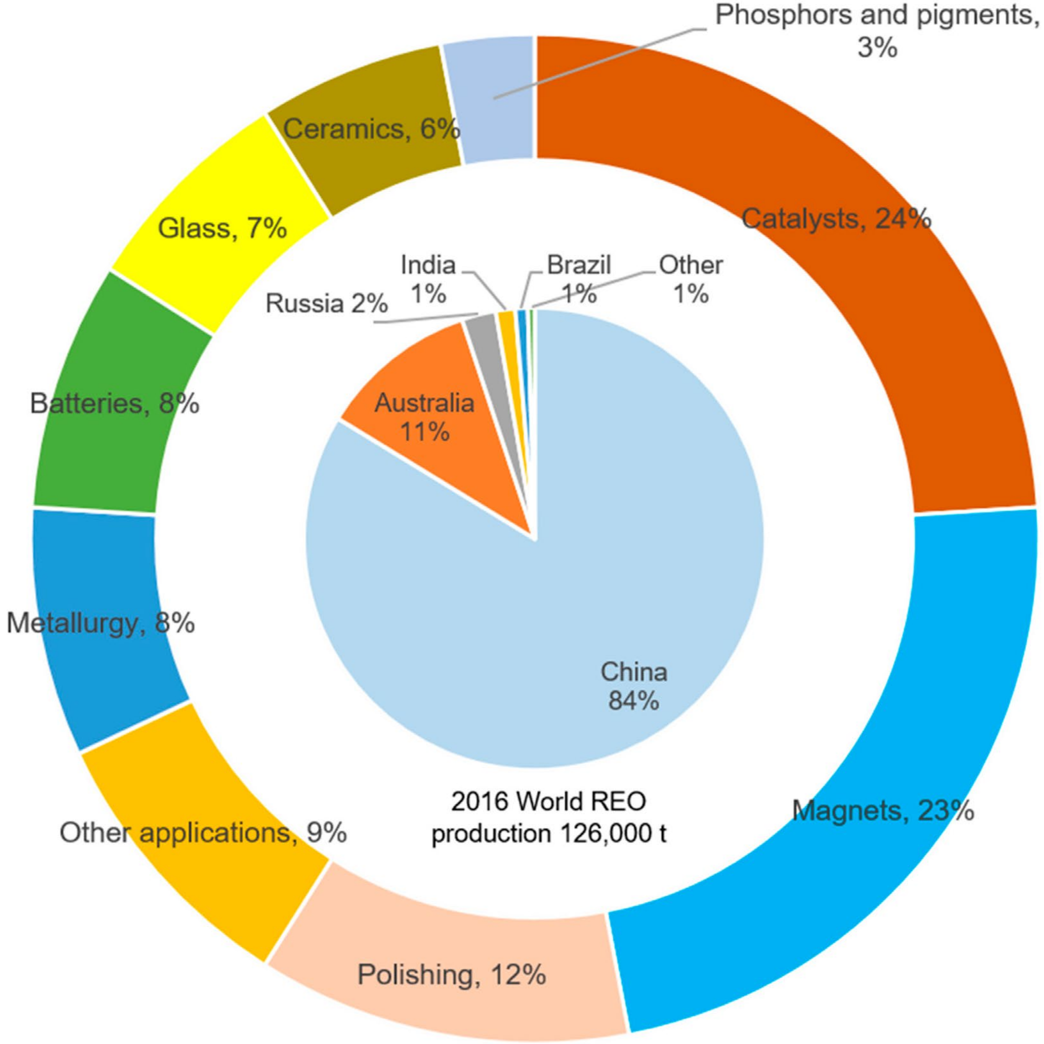
- Interdisciplinary with other department and universities.
- Internationally recognized faculty with many honors and awards.
- Highly regarded by industry and all of our graduates find suitable employment.
- Offering established and well attended Professional Development Short Courses in Mineral Processing and Recycing.
- Founded the Center for Resource Recovery and Recycling: IUCRC
- Participated in Critical Materials Institute

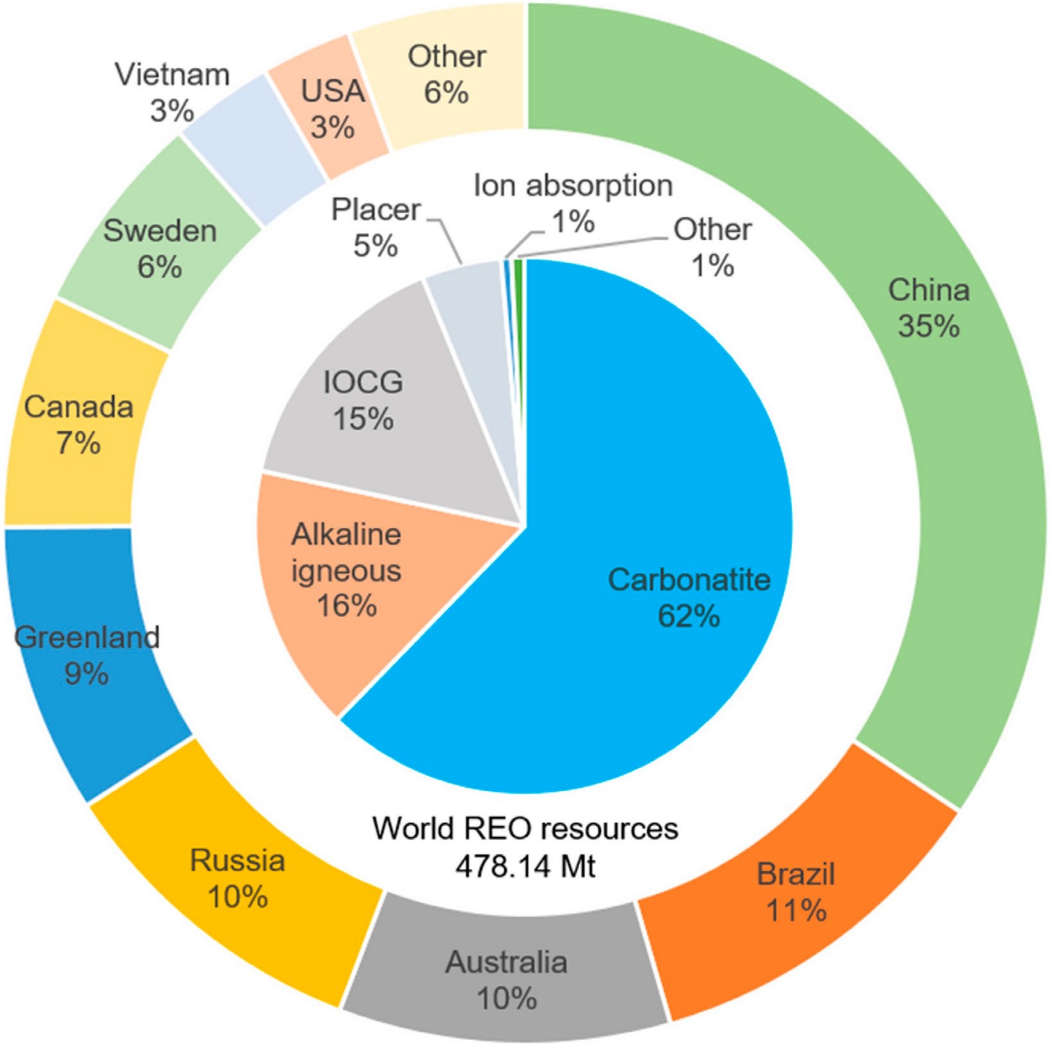
Relevant Projects

- CORE-CM – Three regional projects
- Ga, In, & Ge extraction from a byproduct
- Recovery of Critical Materials and Enhanced Separation
- Bioleaching of Metals from various resources
- Molten Salts purification and Electrolysis

Extractive Metallurgy of Magnet Materials







Global RE production and consumption.

Global RE deposit type and country

Reduction

- Rare Earth Oxides
  - Products from ore processing and separation
  - Starting materials for conversion to metal
  - Very stable and difficult to reduce to metal

How to make it easier?

- RE Oxide → RE Halide → RE Metals
- Fused salt electrolysis
- Making an alloys from which RE metal can be recovered

Reduction

$$MX_n + iR = M + iRX_{n/i}$$

X: O, F, or Cl
R: Reducing agents (e.g. H, C, Li, Na, K, Mg, Ca, Al)

- Metallothermic reduction

$$M(I)X_n + iM(II) = M(I) = iM(II)X_{n/i}$$

  - *Ca: reduces RE Oxides and Fluorides*
  - *K, Na, Li: reduce RE chlorides*
  - *H: cannot reduce RE chloride*
  - *C: reduces RE oxides*

Reduction

- Rare Earth ***Chloride*** system
  - Dehydration of hydrated RE chloride
  - Direct conversion to anhydrous chloride
- Lithium Reduction of Dysprosium, Holmium, and Erbium Chlorides
  - Anhydrous chlorides were reduced at 900^{o}C with pure Li or Li-5% Ca
  - In a tantalum crucible with retort
- It could be 99.94% from anhydrous chlorides
- Process is feasible but:
  - Hygroscopicity and volatility
  - Fluoride system has an advantage

Reduction

- Rare Earth ***Fluoride*** system
  - Wet method

$$RE_2O_3 + 6HCl_{(aq)} \rightarrow 2RECl_3 \cdot xH_2O$$
$$RECl_3 \cdot xH_2O + HF \rightarrow REF_3 \cdot x'H_2O$$
$$REF_3 \cdot x'H_2O \xrightarrow[300^oC\ in\ vacuum]{} REF_3 + H_2O$$

  - Dry method in rotary batch or fluidized bed

$$RE_2O_3 + 6HF \xrightarrow[700^oC\ 8h]{} 2REF_3 + 3H_2O$$
$$RE_2O_3 + 6NH_4F\ HF \xrightarrow[300^oC]{} 2REF_3 + 6NH_4F + 3H_2O$$

- Fluoride purification
  - LiF with HF
  - YF_3 and MgF_3
  - Topping: HF-Ar atmosphere.

Reduction

- $CeF_3 + 3Li \rightarrow 3LiF + Ce$
- $3Ca + 2REF_3 \rightarrow 3CaF_2 + 2RE$

- $SmCl_3$ + Na metal – Mechanical alloying → Sm metal and NaCl

Oxide Reduction Processes

Reactant	Process	Results
RE_2O_3-Mg (Nd, Gd)	REO in molten Mg @1050^{o}C	Mg-RE alloy (low grade)
RE_2O_3-La (Sm)	Reduction-distillation in Ta crucible and condenser	Pure metal condensate
RE_2O_3-La (Dy)	Reduction-distillation	Residual La, O in condensate
RE_2O_3-La (Sm)	Reduction-distillation in Mo crucible and Ta condenser	Pure metal condensate
RE_2O_3-La (Sm) RE_2O_3-Th (Nd, Gd, Dy)	Reduction-distillation in Mo crucible and Ta condenser	Pure metal condensate
Sm_2O_3-C	Reduction-distillation	Impure Sm condensate
Sm_2O_3-Ca	Reduction-distillation	Sm containing Ca
Gd_2O_3-$CaCl_2$-Mg	Heated to reaction temperature and slag leached off	Gd metal powder
Nd_2O_3-Ca Nd_2O_3-Na	$CaCl_2$-NaCl bath and metal extracted by Nd-Zn or Nd-Fe alloy pool	Nd-Zn or Nd-Fe alloy

Reduction

Conditions for Reduction-Distillation Procedure and Efficiency

Metal Oxide	Reductant	Temp (°C)	Crucible	Efficiency (%)
Pr	Th	1900-2000	Ta	75
Nd	Th	1950-2000	Ta	75
Sm	La	1300-1350	Ta	78
Gd	Th	1900-1950	Ta	75
Dy	Th	1750-1800	Ta	80

Other Reduction Procedure

- Metallothermic Reduction

$$Nd_2O_3 + 3Ca \rightarrow 3CaO + 2Nd$$

- Carbothermic Reduction
- Electrolytic Production of RE Metals
- Recovery of RE Metals as Alloys

Refining

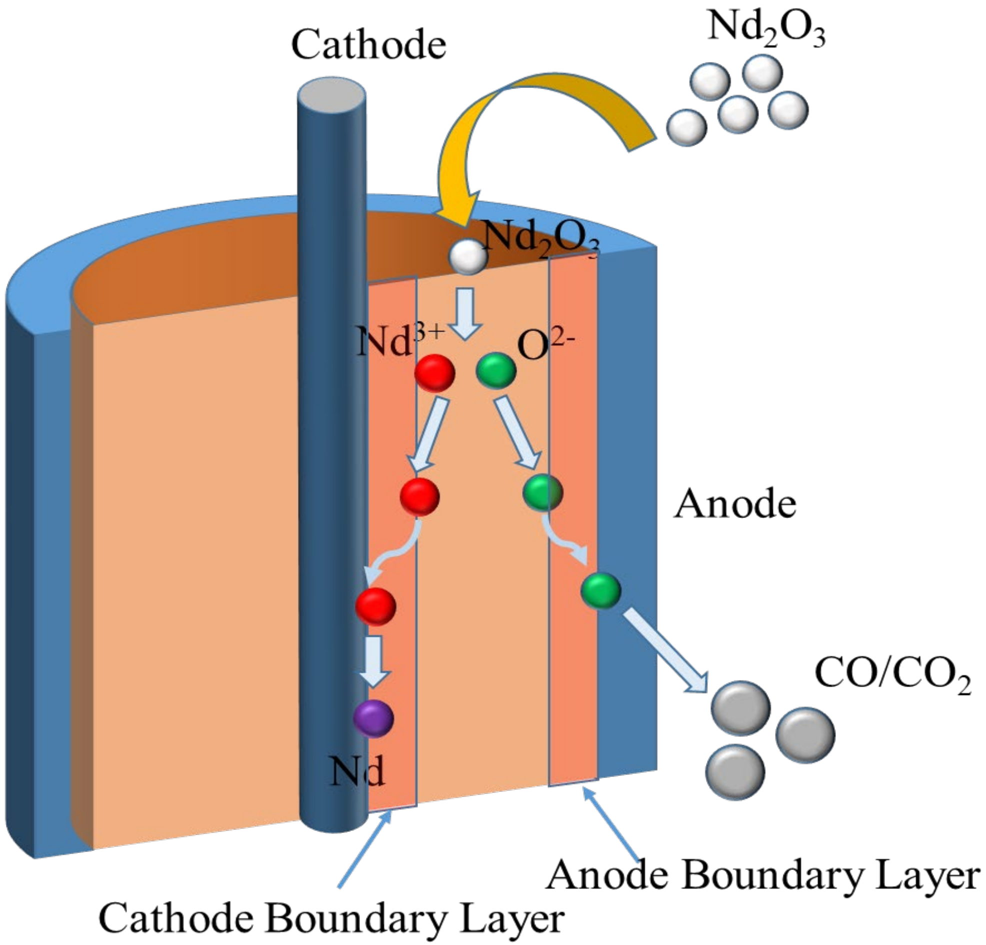
- Reduced RE metals: 98-99%
- It is more economically viable to produce impure metal and further refine it.
- Origin of impurities
  - As-reduced starting materials (alloying element)
  - Crucible (Ta) – 0.05% Ta in as-reduced.
  - Carbon from graphite anode
  - Environment – controlled or air

Refining

- Methods for Impurity removal
  - Pyrovacuum treatment
    - Distillation
    - Halogen/halide removal
    - Degassing
  - Electrorefining
    - Gd: 77.6%LiCl, 11.2%LiF, and 11.2%GdF_3
      - LiCl, LiF lower mp of the mixture
      - Cathode: pure Gd rod, Anode: impure Gd to be refined
    - Gd: 65% LiF & 35% GdF_3
      - Cathode: Ta rod, Anode: impure Gd to be refined
  - Zone Refining
  - Solid State Electrolysis/Solid State Electrotransport: Nd,Pr,Gd,Tb,Dy,Sm
  - ZR followed by SSE: Nd,Gd,

- Y, Gd, Tb, Lu
- Sc, Dy, Ho, Er, Lu
- Sm, Eu, Tm, Yb

Study @CSM



Desirable overall reaction

$$\frac{1}{2}Nd_2O_3 + \frac{3}{4}C = Nd + \frac{3}{4}CO_2(g)$$ **E = -1.4 V**

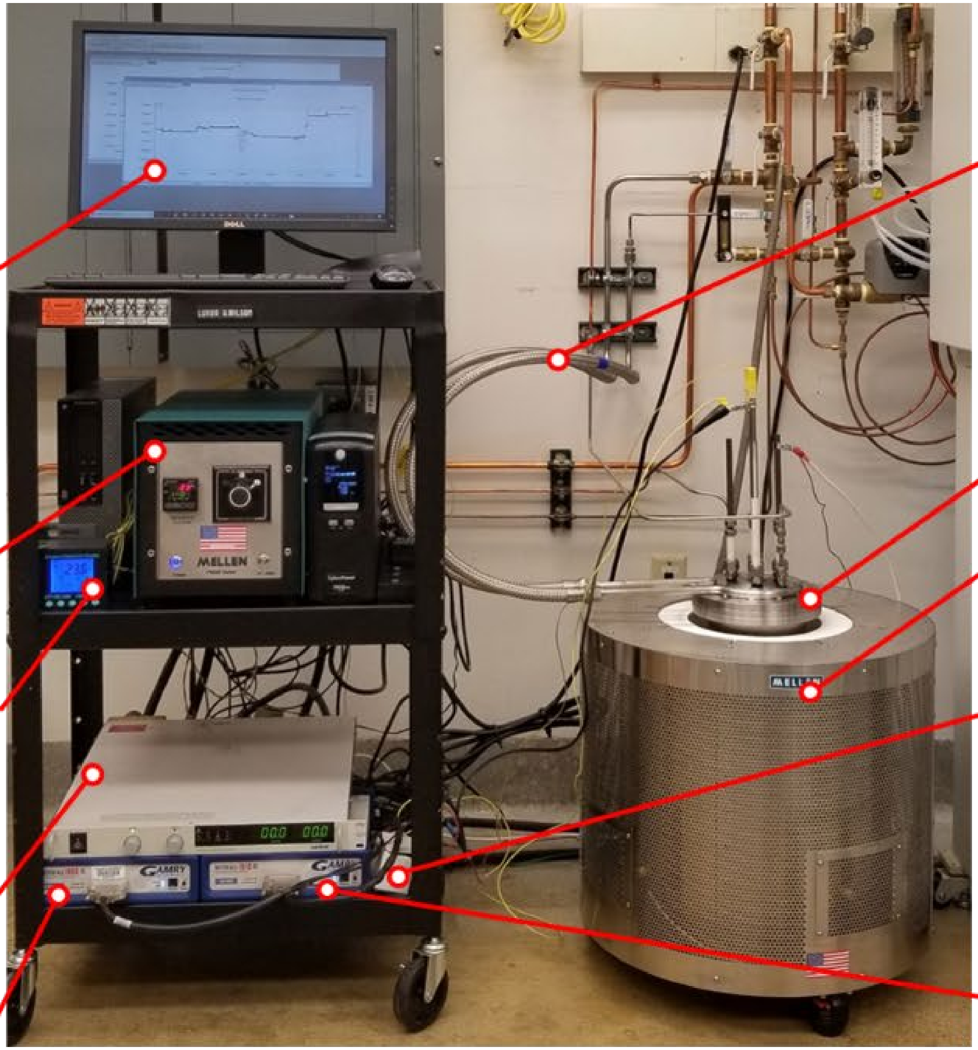
Secondary overall reaction

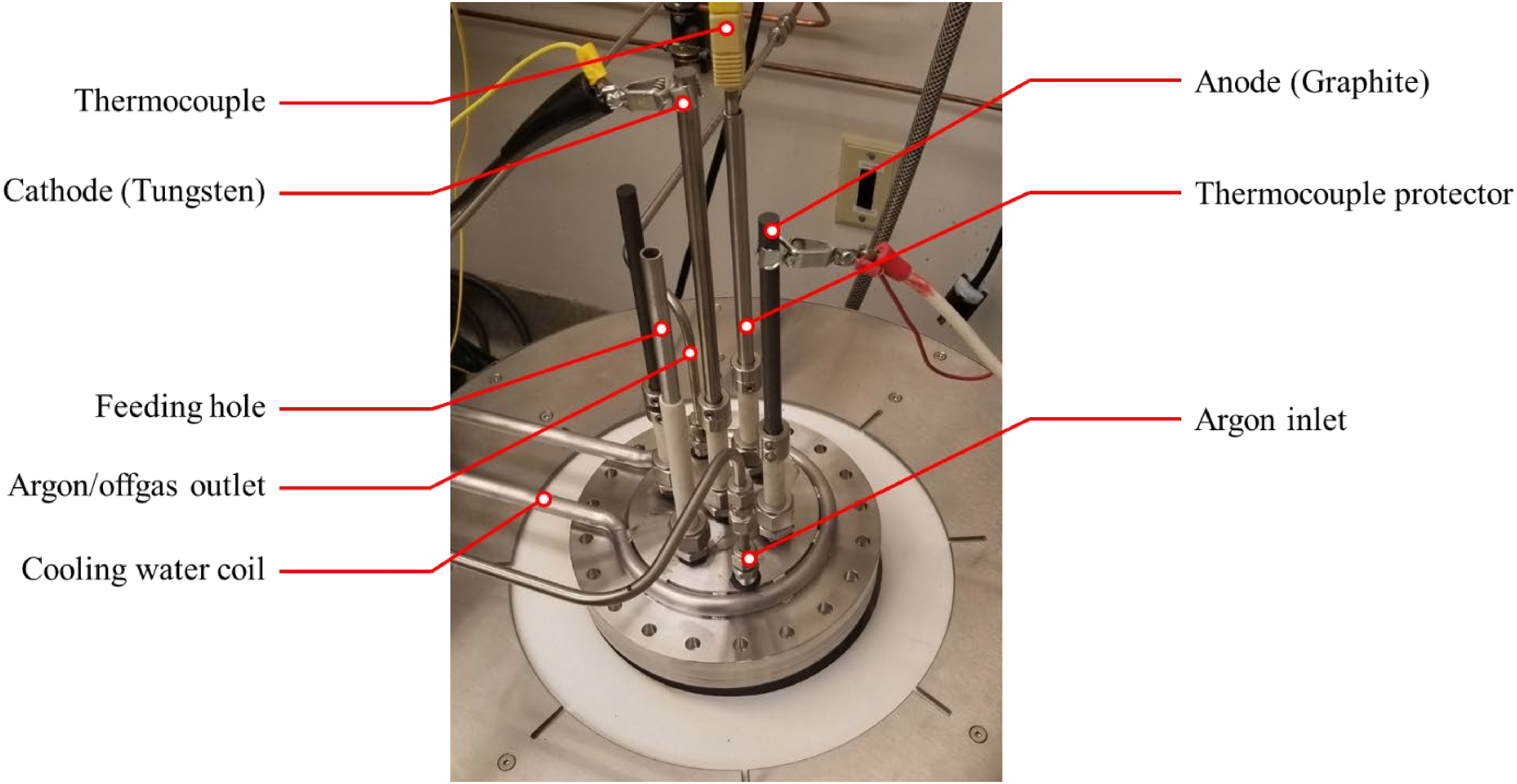
$$\frac{3}{4}C + NdF_3 = Nd + \frac{3}{4}CF_4(g)$$ **E = -2.8 V**

Half cell reactions

Anode: $2[O^{2-}] + C = CO_{2(g)} + 4e$

Cathode: $Nd^{3+} + 3e = Nd$


Data logging
Furnace controller
Temperature scanner
Power supply
Potentiostat I
(voltage for cell)
Cooling water
Electrolysis cell
Tubular furnace
Shunt for current determination
Potentiostat II
(voltage for shunt)


Thermocouple
Cathode (Tungsten)
Feeding hole
Argon/offgas outlet
Cooling water coil
Anode (Graphite)
Thermocouple protector
Argon inlet

Where We Are Now?

- Who makes magnets?
  - Magna Quench – Neo Material
  - Electron Energy Corporation

- What do we need?
  - Supporting effort outside of China
  - Continuous support and contract even if its cost is higher than that of China
  - Define the best way to compete against Chinese technology/policy.

- Opportunity
  - Monazite concentrate
  - Heavy Mineral Sands
  - [U, Th] $\propto$ [RE]

- Risk
  - Many project under development
  - When are we getting a product?
  - ***PERMIT***

Thank You !!!

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