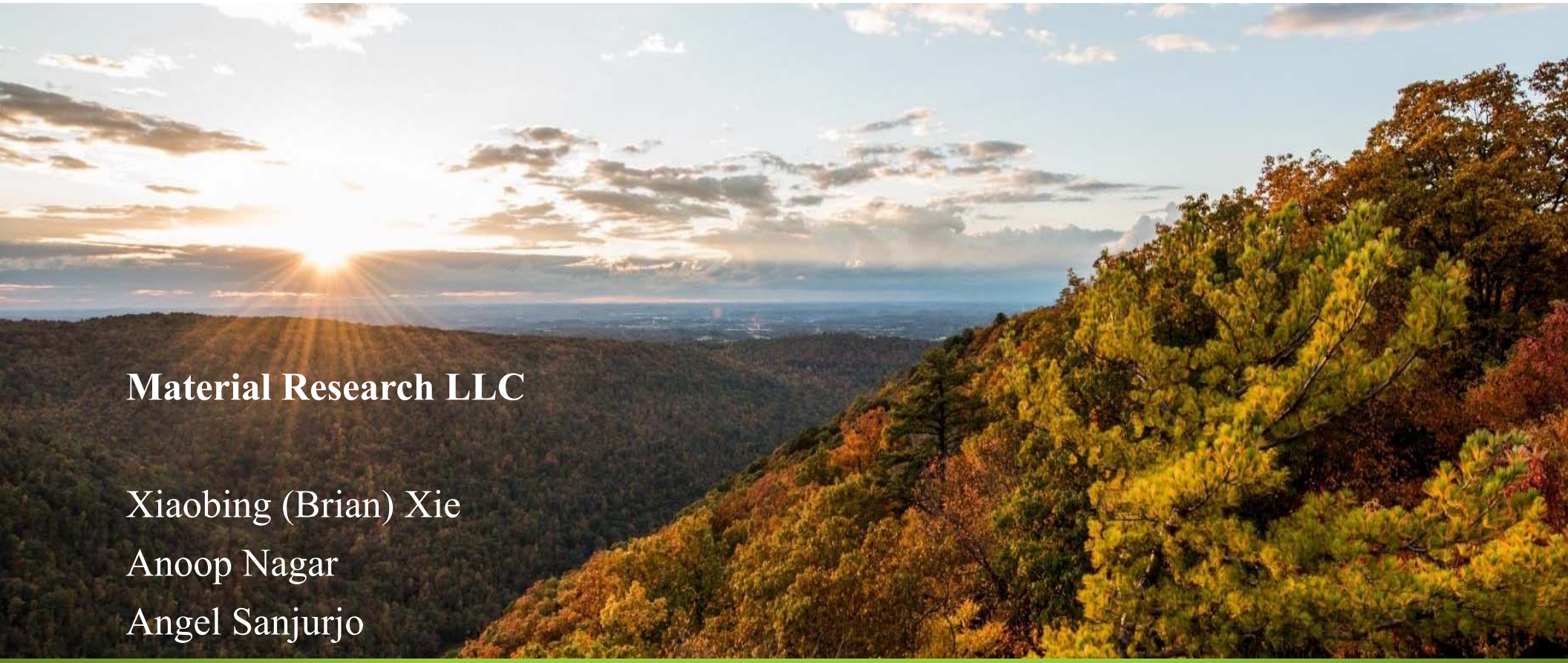
SILICON-CALCIUM BASED REDUCTION OF RARE EARTH OXIDES



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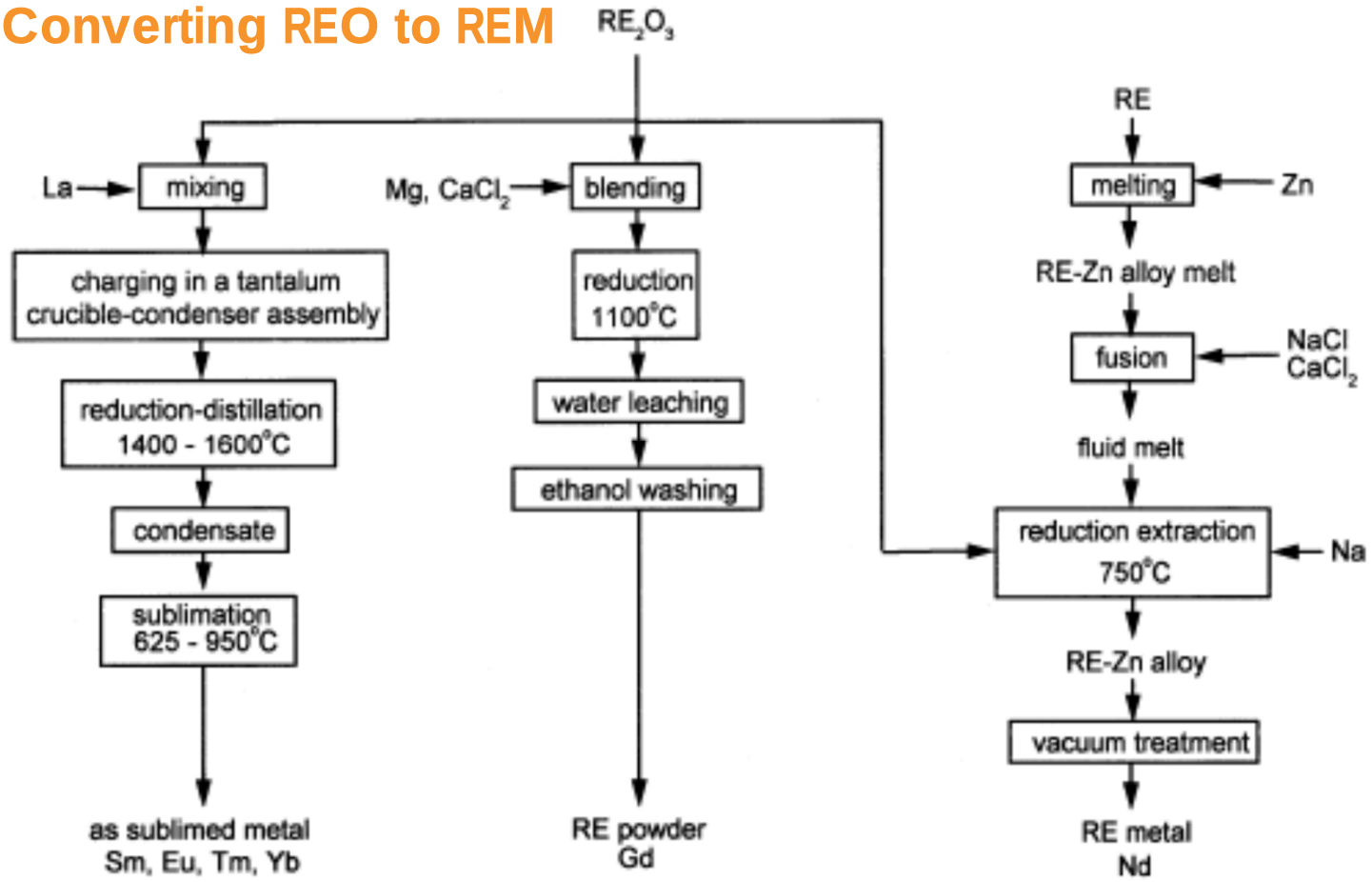
Needs and Challenges

Converting REO to REM

- Need to develop domestic supply sources of Rare Earth (RE) elements.
- Recovery of rare earth oxides (REOs) from coal ash or coal byproduct is being spearheaded by DoE.
- Current processes for commercial production of rare earth metals are inefficient and tedious and most involve converting RE ores (oxide) to anhydrous RE chlorides or fluorides.
- Developing new or improved processes that directly reduce REOs to RE metals or RE alloys can potentially simplify and lower cost of REM production.

Technology Benchmark and Limitations

Converting REO to REM

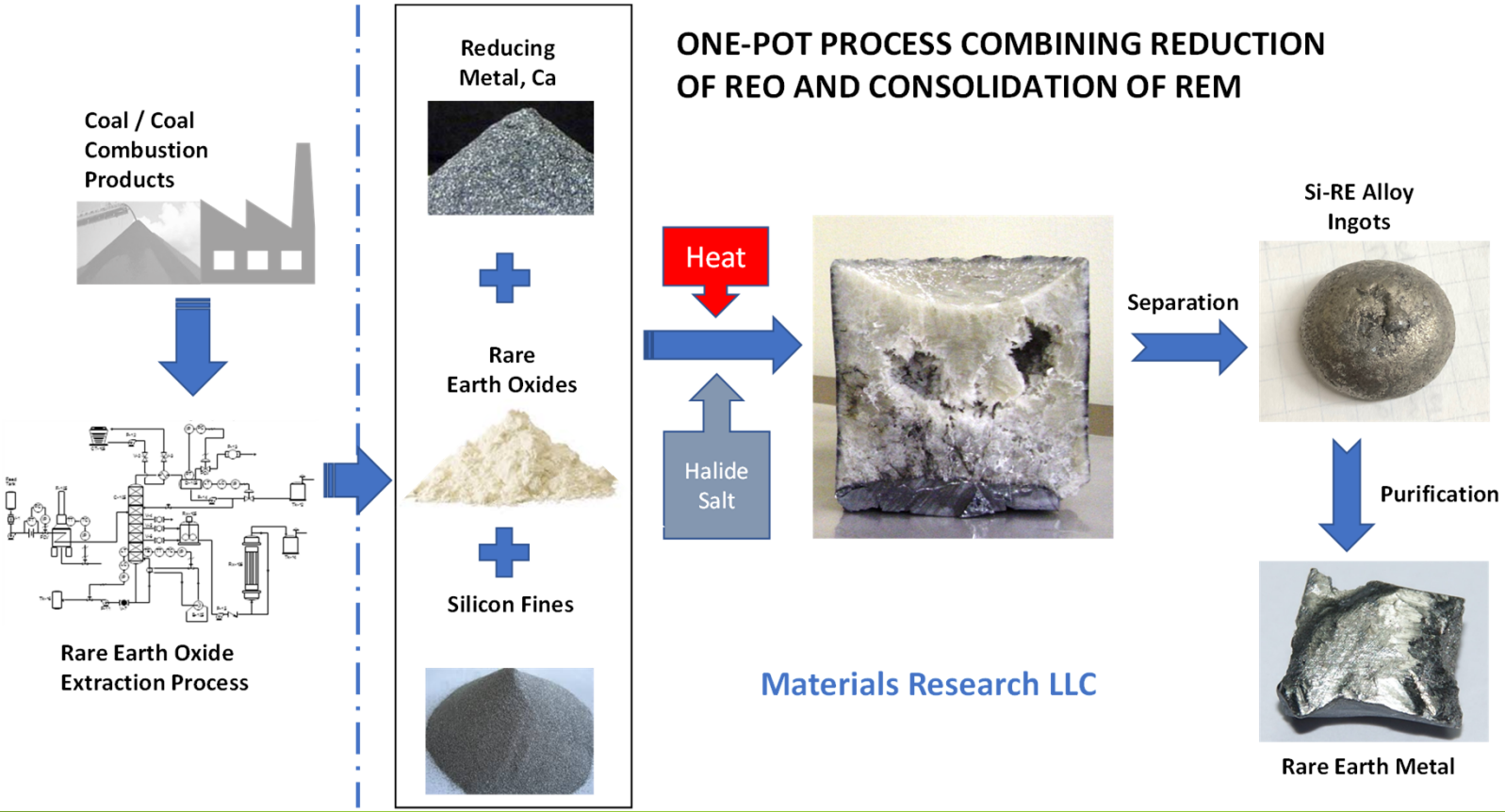


- Slow reduction kinetics due to diffusion barrier
- Expensive La metal used as reducing agent to reduce REOs (limited to volatile REEs, Sm, Eu, Tm, Yb)
- Separation REM from byproducts is difficult and tedious.

Project Description and Objectives

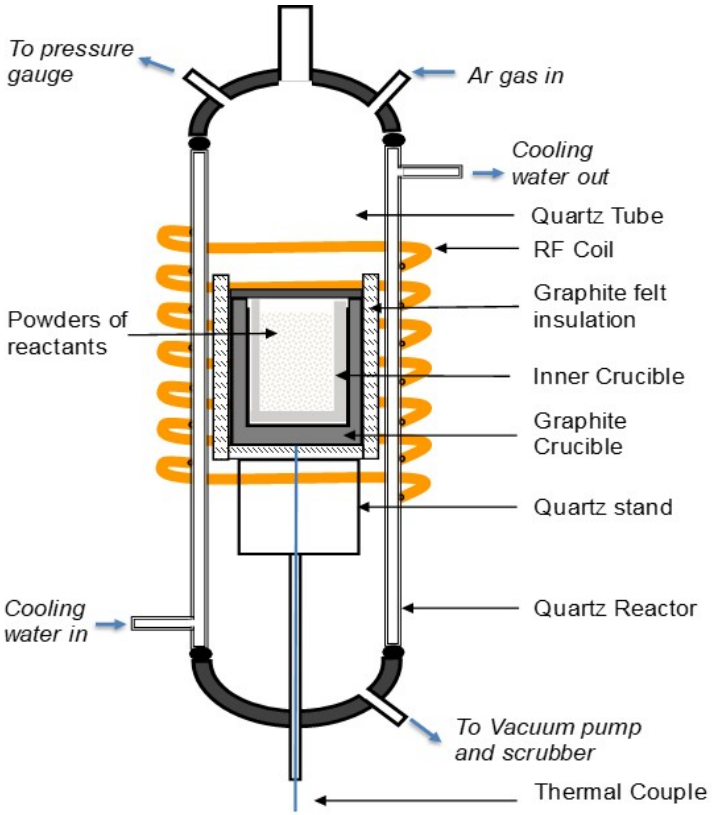
NATIONAL ENERGY TECHNOLOGY LABORATORY

Developing a new process to facilitate REO reduction and REM separation



Project Update

Reactor Setup and Materials



- REO (including Nd_2O_3, Sm_2O_3, Eu_2O_3, Dy_2O_3 and Er_2O_3) are reduced by Ca/Si.
- Ca shot (~1 mm) is the main reductant.
- Silicon fines, obtained from solar industry wastes.
- Molten alkaline earth metal halide is the reaction medium

Technical Studies

$$RE_2O_3 + 3Ca + Si\ (\text{in excess}) = 3CaO + 2RESi_x\ (\text{in Si})$$

Nd_2O_3 powder is used as the model compound to demonstrate feasibility of reduction and product separation, studies including:

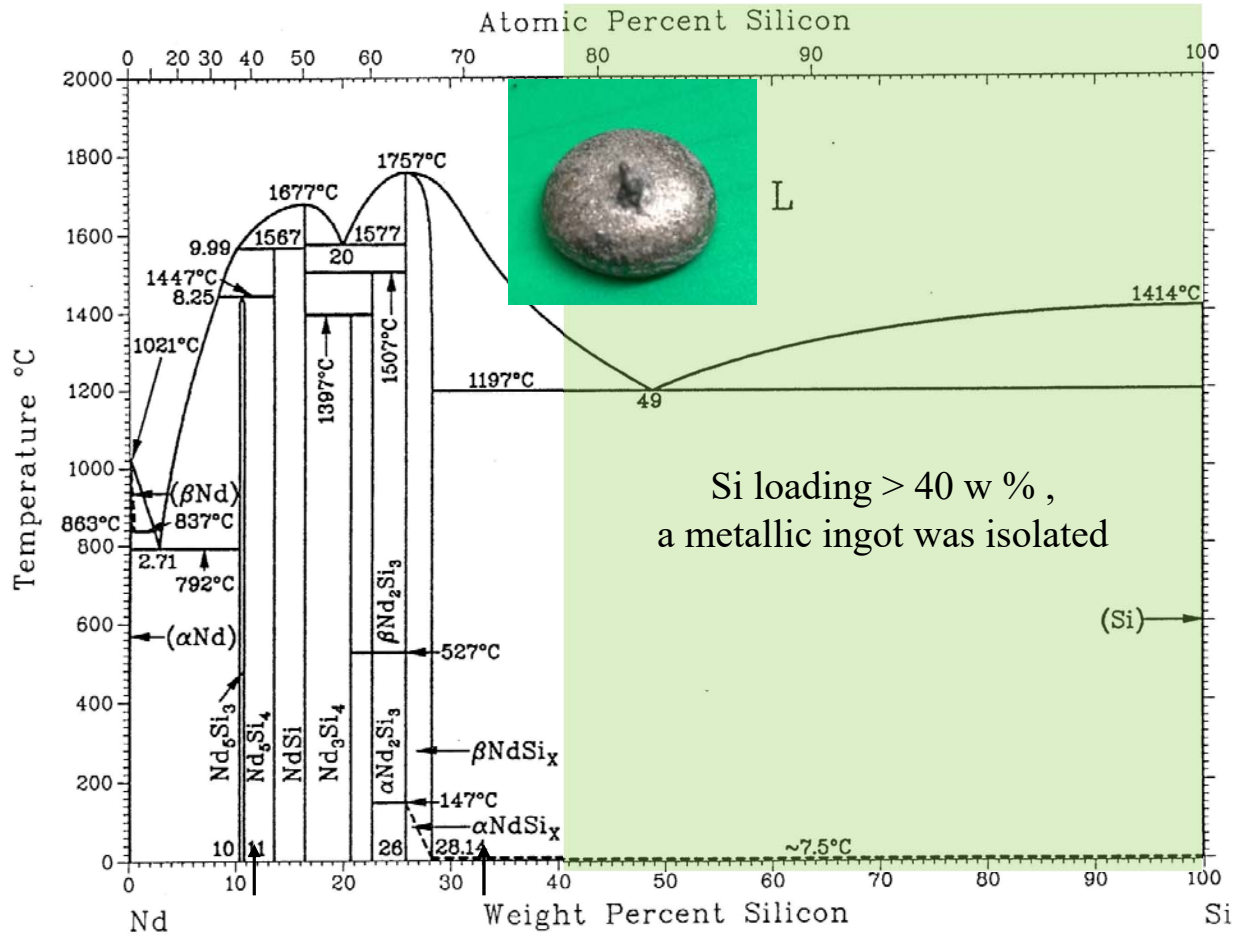
a) Selection of Crucible and Liner Materials
b) Selection of Molten Salt Media
c) Test Various Si Loadings
d) Optimize Experimental Procedure

The optimized procedure is then applied to the reduction of other REO's, including **Sm_2O_3, Er_2O_3, Dy_2O_3, and Eu_2O_3**.

Si-Assisted Calciothermic Reduction of Nd_2O_3 Various Si Loading

Si loading Si/(Si+Nd)	0%	0%	~13 wt %	~34 wt %	> 40 wt%
T_{max} (°C) Time (hours)	< 1200 2	1300 2	1300 2 hrs 1420 1 hr	1300 2 hrs 1420 1 hr	1300 2 hrs 1420 1 hr
Product appearance	One small ball and black powders	Black powders	A mixture of metallic and ceramic powders	One grey sintered disk 	One metallic ingot 
Nd recovery yield	NA	NA	~60%	~99%	~99%
Note	Nd powder re-oxidized in air	Nd powder re-oxidized in air	$NdSi_x$ and $NdAlO_3$	$NdSi_2$ and Si, stable in air	$NdSi_2$ and Si, stable in air

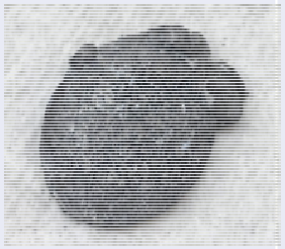
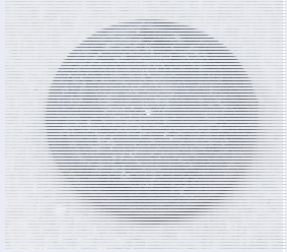
Nd-Si Phase Diagram



The Role of Silicon Fines

- Ca reacts first with Si fines to form distributed $CaSi_2$
  - Providing large reactant surface area,
  - bringing Ca in close contact with the REO powder and,
  - minimizing Ca loss as vapor at high temperature
- REM and Si droplets are formed during consolidation. Molten Si scavenges and dissolves REM forming a metallic ingot of RE-Si alloy that coalesces and separates from the byproduct CaO.
- Forms stable rare earth silicide (*e.g.*, $RESi_2$, $-\Delta H^o_f$ 60-70 kJ/mol), also helps to avoid oxidation in air or reaction with water facilitating recovery and storage.

Recovery RE-Si Ingot with High Yield

	Nd_2O_3	Sm_2O_3	Er_2O_3	Dy_2O_3	Eu_2O_3	Nd_2O_3 & Eu_2O_3
REM recovery yield	~99%	~96%	~ 99%	~98%	~50%	~70%
Si-RE alloy						

High recovery based on mass balance was achieved with Nd, Sm, Dy, and Er, low recovery for Eu is due to reactivity of Eu with the chloride molten salt

Separation of REM from RE-Si Alloy

Pure metal	Eu	Sm	Si
Vapor pressure at 1500ºC, atm	0.85	0.20	1.4×10^{-6}

We tried to vapor transport the volatile REE from the RE-Si alloy at high temperature using vacuum distillation method.

However, rare earth silicides are too stable to be thermally decomposed at ~1500°C, predominantly the excess Si in RE-Si ingot was transported to the cooler end of the reactor.

Technological challenges

Separation of REM from RE-Si alloy via hydride formation

- $RESi_2\ (c) + 3H_2\ (g) = REH_2\ (c) + 2SiH_4\ (g)\uparrow$

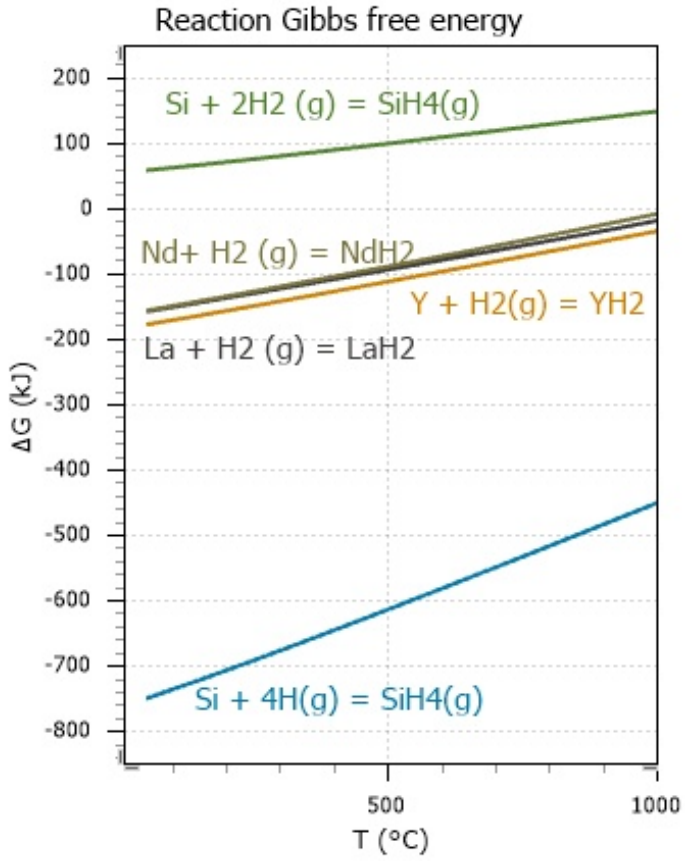
  $\Delta G^o > 0$

  Preliminary test of heating RE-Si ingot in hydrogen atmosphere did not result in the formation of metal hydrides.

- $RESi_2\ (c) + 6H\ (g) = REH_2\ (c) + 2SiH_4\ (g)\uparrow$

  $\Delta G^o < 0$

  Atomic hydrogen (via H_2 plasma or Pd catalyst) may be able to produce SiH_4 gas and result in separation of REM from Si



Preparing Project for Next Steps

Preparing Project for Next Steps

Market Benefits/Assessment

- Universal and efficient processes for converting REO to RE metals or alloys are needed.
- This one-pot calcio-thermic reduction process circumvents the kinetic limitations as well as facilitate easy product separation, and thus provides a simple and efficient approach to convert REO to RE-Si alloys.
- For applications that use $RESi_x$, the process is directly applicable.
- For markets that need pure RE metals, a further separation is needed.

Preparing Project for Next Steps

Technology-to-Market Path

- Converting RE-Si alloy to SiH_4 gas and REH_2 with H_2 plasma or a catalyst may be a route to separate Si from REE
- Demonstrate this process on all other REOs as well as mixture of REOs
- Explore other alloying metals besides Si
- Scale-up and semi-continuous process development
- Work with industrial partners to scale up the process to a pilot plant and commercialization

Concluding Remarks

Conclusions and Achievements

Si-Assisted Calciothermic Reduction of RE_2O_3

- Si fines react with Ca first to form Ca silicides thus distributing Ca efficiently on REO's surface and prevents Ca loss via vaporization.
- Above melting point of Si, excess molten Si scavenges and dissolve $RESi_x$, and coalesce into an ingot of Si-RE alloy.
- The halide molten salt dissolves CaO, and facilitates the coalescence of Si-RE alloy droplets into a single pool, resulting in easy separation from the byproduct slag.
- A one-pot process consisting of a single step of heating RE_2O_3-Ca-Si mixture to 1420ºC in a molten salt, combines reduction and consolidation. This process is inexpensive and efficient way to reduce REO and produce Si-RE alloys.
- Near full recovery yield of RE in the form of Si-RE alloy ingot was achieved for Nd, Sm, Dy and Er oxides, while the recovery yield was ~50% for Eu. This protocol is potentially universal for all REO as well as REO mixture.

Next steps

Process further developments

- Separation of REM from the RE-Si alloys
- Explore potential markets and applications for RE-Si alloys
- Explore other alloying metals besides silicon in calciothermic reduction of REO for improving kinetics and extracting REM
- Explore with mixture of REO extracted from coal ashes
- Scale up and commercialization development

Acknowledgement

Thank you for your attentions !