Critical Mineral Extraction from Waste Streams: Li, REE, Ni, and V

Jinichiro Nakano
Technical Fellow
Research & Innovation Center
NATIONAL ENERGY TECHNOLOGY LABORATORY

Presented to the Critical Mineral Workshop 2021 (Virtual-Oklahoma)

Nov. 8 – 10, 2021

Disclaimer

This project was funded by the Department of Energy, National Energy Technology Laboratory an agency of the United States Government, through a support contract. Neither the United States Government nor any agency thereof, nor any of its employees, nor the support contractor, nor any of their employees, makes any warranty, expressor implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Authors and Contact Information

Jinichiro Nakano and Anna Nakano

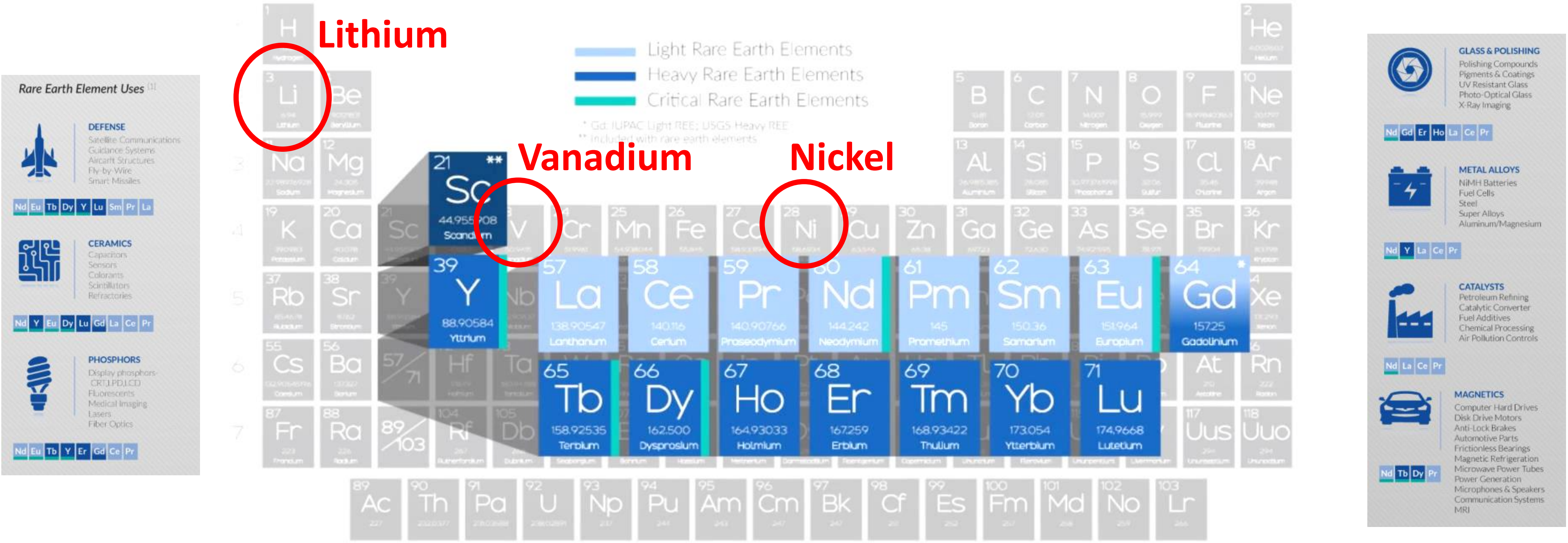
National Energy Technology Laboratory, 1450 Queen Avenue SW, Albany, OR 97321, USA

NETL Support Contractor, 1450 Queen Avenue SW, Albany, OR 97321, USA

Critical Elements: REE, Li, Ni, and V

NATIONAL ENERGY TECHNOLOGY LABORATORY

Clean energy applications



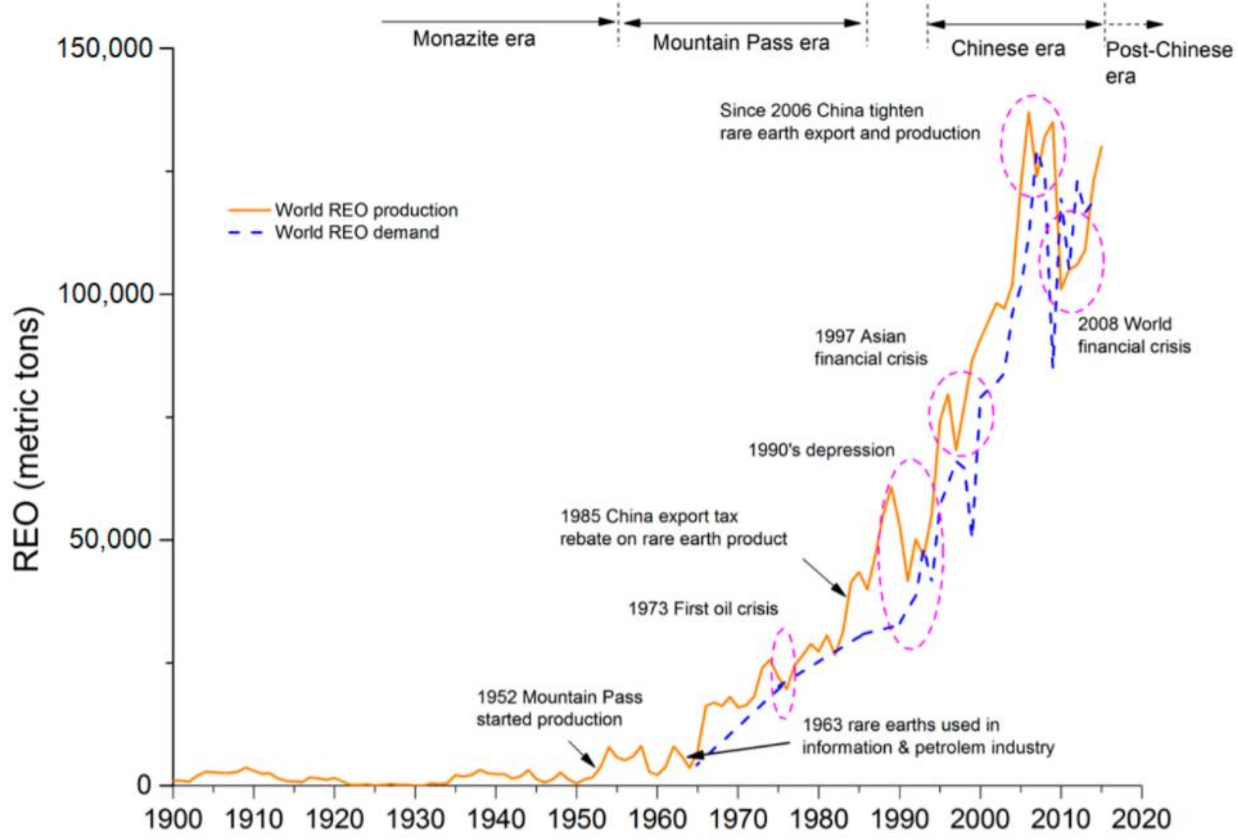
https://www.netl.doe.gov/research/coal/rare-earth-elements

Rare Earth Elements

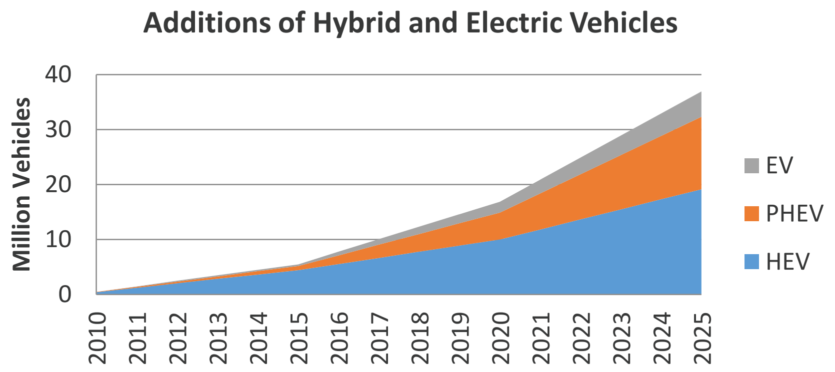
Rare Earth Elements (Demand)

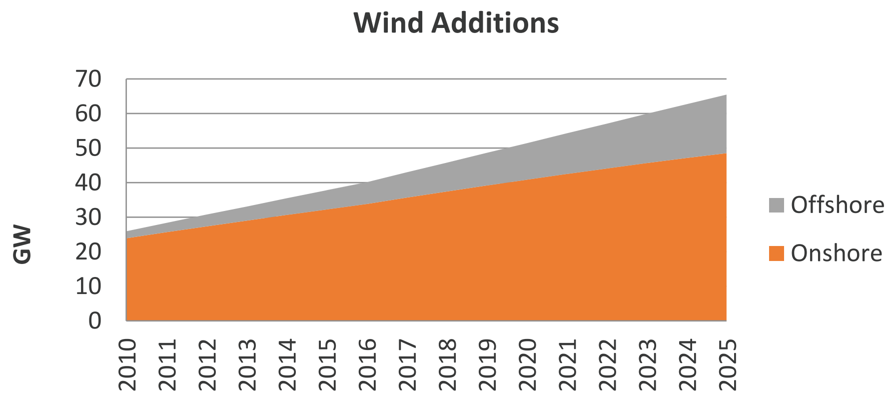
NATIONAL ENERGY TECHNOLOGY LABORATORY

- $120 million imported into the U.S. in 2016



Zhou, et al., Minerals 2017, 7, 203

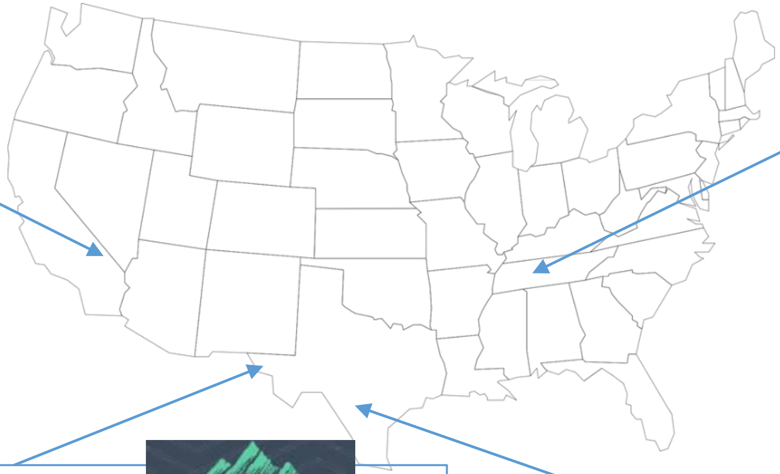




DOE's Critical Materials Strategy 2010

U.S. REE Production/Projects Status

MP Materials
- NY listed in November 2020
- The only active U.S. REE mine (Mountain Pass, CA)
- Focus on ***LREEs***
- ~10% owned by Shenghe Resources
    - Buys all of MP REE concentrates and process in China



Titan Project
- Total Mineral Resource of 431Mt @ 2.2% Total Heavy Minerals ("THM")
- High value THM assemblage of 12% zircon, 10% rutile, 40% ilmenite and 2% REE concentrate with an excellent ratio of heavy and light rare earths

USA Rare Earth
- NY listing in 2021 (plan)
    - \$1.56 billion valuation
    - \$350.4 million capital (1.4 yr payback)
- The Round Top project in Sierra Blanca, Texas
    - Partner with Texas Mineral Resources Corp
    - 20,000 t/day mining
    - 2212 t/y REO production
    - > 100 years supplies
    - Focus on ***HREEs*** (70%)
- Also intends to mine lithium
    - 8956 t/y Li_2CO_3 production

Lynas
- Australian miner, the largest REE operation outside China
- \$30 million funded by the Pentagon
    - Plans a ***LREE*** processing plant in Hondo, Texas
    - Would produce 1/4 of world supply

Rare Earth Elements (Production)

- Mining naturally-occurring REE ores/sand: monazite, xenotime, etc.
- Excavation, crushing, separation, acid leaching


Monazite ore

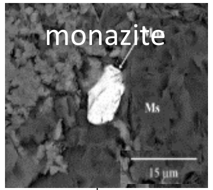

monazite sand

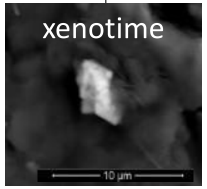

mining

Prices of REE ores: $ 500 - 116,000 per ton (vs. $ 70 per ton for iron ores)

Molten 2021, Nakano et al.

More REEs Resources? → Coal By-Product





Tens ppm REEs

Power plants

Steelmaking plants

Industrial waste

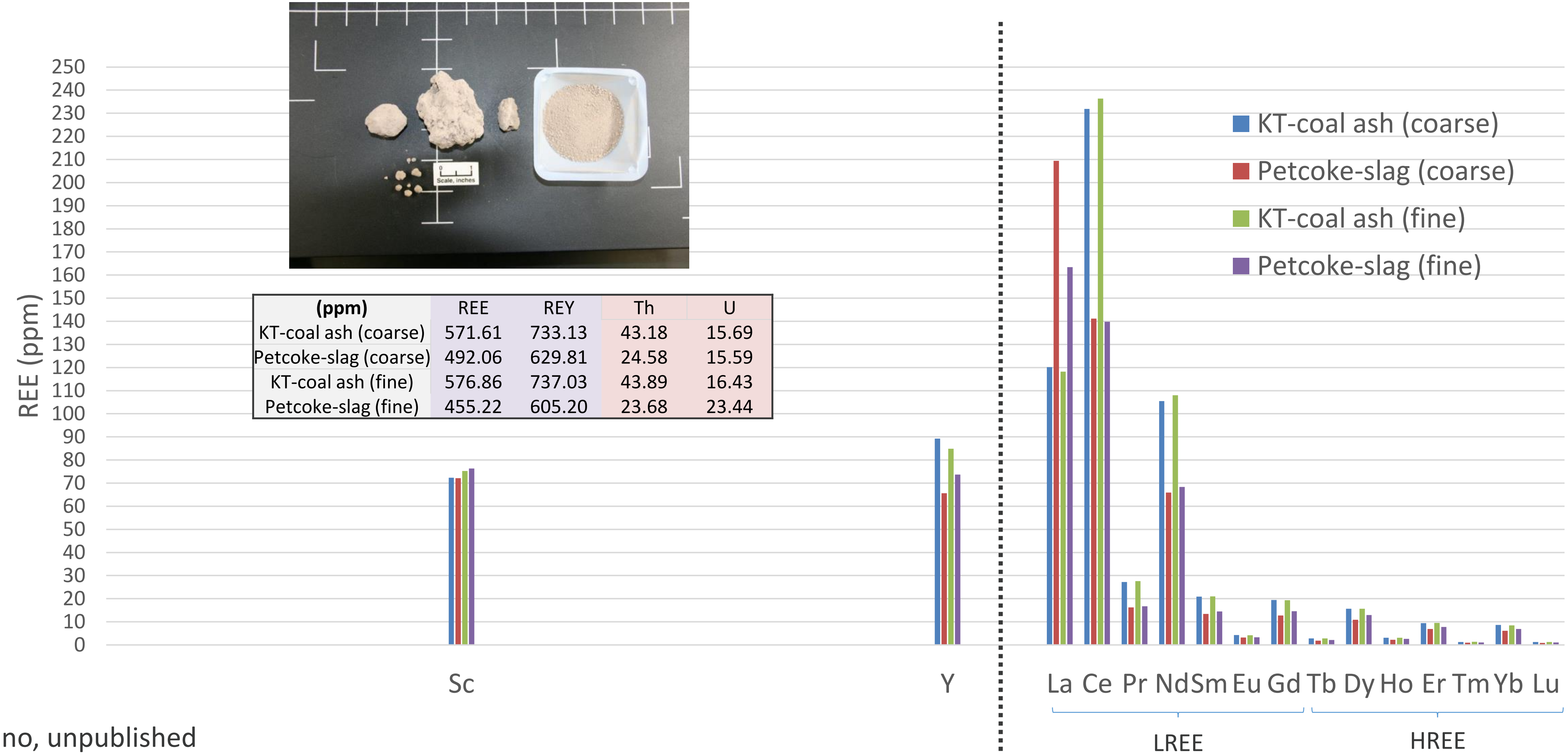
hundreds – thousands ppm REEs

Can we recover REEs?

Advantages: Already out of the ground + Abundant + Cheap + Environmental

Molten 2021, Nakano et al.

REEs in Coal Ash and Petcoke Slag

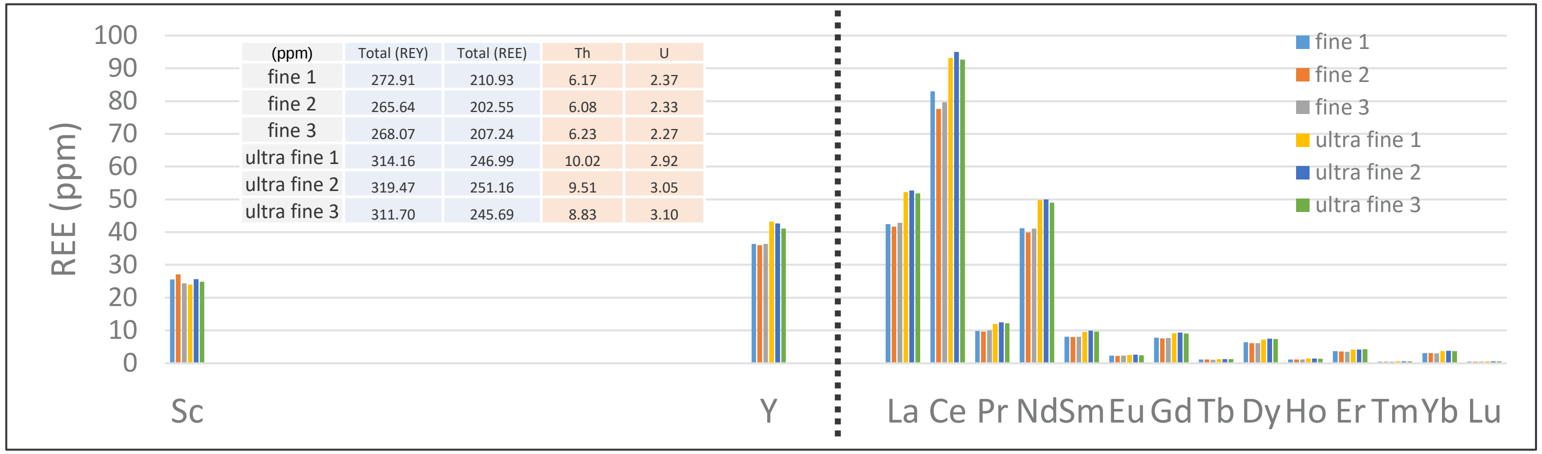


(ppm)	REE	REY	Th	U
KT-coal ash (coarse)	571.61	733.13	43.18	15.69
Petcoke-slag (coarse)	492.06	629.81	24.58	15.59
KT-coal ash (fine)	576.86	737.03	43.89	16.43
Petcoke-slag (fine)	455.22	605.20	23.68	23.44

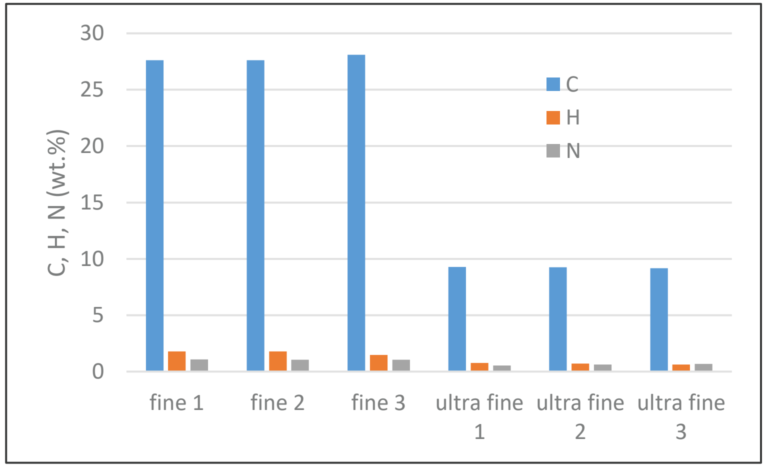
Nakano, unpublished

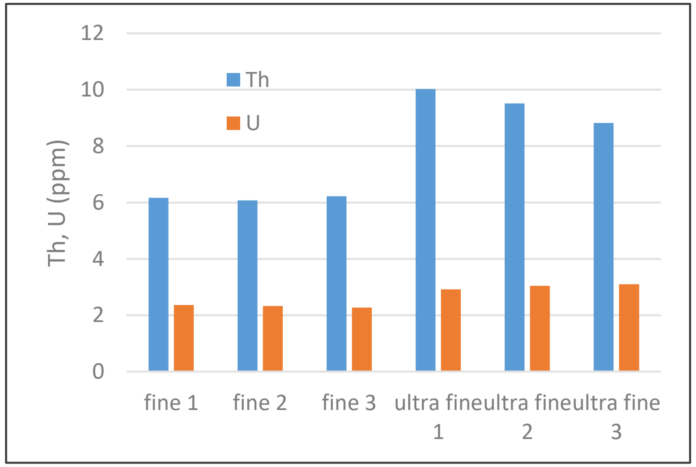
REEs in Biomass

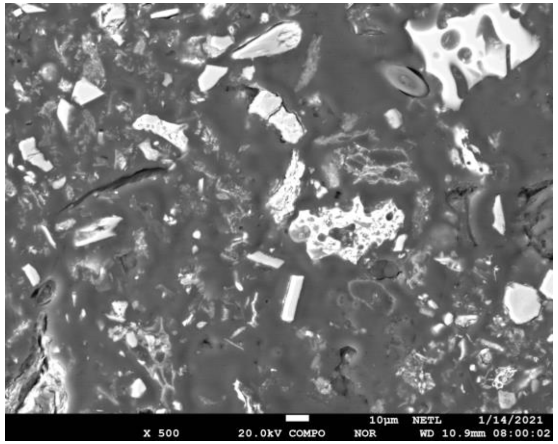
- Historical wildfires on West Coast produced fly ash in summer of 2020.
- More than 1.2 million acres burned in OR alone.



(ppm)	Total (REY)	Total (REE)	Th	U
fine 1	272.91	210.93	6.17	2.37
fine 2	265.64	202.55	6.08	2.33
fine 3	268.07	207.24	6.23	2.27
ultra fine 1	314.16	246.99	10.02	2.92
ultra fine 2	319.47	251.16	9.51	3.05
ultra fine 3	311.70	245.69	8.83	3.10







Remarks: Wildfire produced 'separated' crystal particles (recoverable)

Nakano, unpublished

REEs in Plastics

NATIONAL ENERGY TECHNOLOGY LABORATORY

Table 2
Individual and summed concentrations of REEs in each consumer plastic (in mg kg^{-1}). Note that numbers preceded by "<" are sample- and element-specific method detection limits.

Description	Sample	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Sum
Board game	1	0.31	0.28	0.32	0.19	0.039	0.14	<0.05	0.024	0.032	0.006	0.025	0.006	<0.02	<0.005	<0.02	<0.005	1.38
Coat hanger	2	0.33	0.21	0.50	0.38	0.099	0.38	<0.05	0.096	0.067	0.005	<0.02	<0.005	<0.02	<0.005	<0.02	<0.005	2.07
Tyre cap	3	0.84	0.69	1.49	1.37	0.27	0.94	0.21	0.076	0.18	0.028	0.14	0.028	<0.3	<0.02	<0.3	<0.02	6.27
Poster tube cap	4	<0.2	0.06	0.31	0.13	0.025	0.085	<0.05	0.028	<0.02	<0.005	<0.02	<0.005	<0.02	<0.005	<0.02	<0.005	0.64
Makeup brush handle	5	0.51	0.80	0.83	0.42	0.090	0.33	0.094	0.33	0.088	0.015	0.077	0.017	0.048	0.008	0.044	0.008	3.71
Makeup brush bristles	6	<0.3	<0.03	1.04	<0.03	<0.005	<0.03	<0.05	<0.005	<0.07	<0.015	<0.07	<0.005	<0.3	<0.005	<0.3	<0.005	1.04
Bag handle	7	<0.2	0.051	<0.2	0.095	0.022	0.072	<0.05	0.068	<0.02	<0.005	0.068	<0.005	<0.02	<0.005	<0.02	<0.005	0.38
Timer switch casing	8	<0.2	<0.02	<0.2	<0.02	<0.003	<0.02	<0.04	<0.004	<0.02	<0.004	<0.02	<0.004	<0.02	<0.004	<0.02	<0.004	<0.60
Torch casing	9	0.54	0.91	2.60	0.96	0.18	0.64	0.14	0.054	0.13	0.021	0.11	0.022	0.060	0.009	0.051	0.009	6.43
Magnifying glass handle	10	0.30	0.96	1.49	1.67	0.41	1.32	0.23	0.24	0.25	0.027	0.24	0.038	0.085	0.014	0.077	0.012	7.37
Games counter	11	0.75	<0.02	<0.2	<0.02	<0.002	<0.02	<0.03	<0.003	<0.02	<0.003	<0.02	<0.003	<0.02	<0.003	<0.02	<0.003	0.75
Water pipe adaptor	12	<0.2	0.078	<0.2	0.048	0.011	0.037	<0.04	<0.004	<0.02	<0.004	<0.02	<0.004	<0.02	<0.004	<0.02	<0.004	0.17
Cocktail stirrer	13	<0.2	0.055	<0.2	0.11	0.022	0.081	<0.05	0.026	<0.02	<0.005	<0.02	<0.005	<0.02	<0.005	<0.02	<0.005	0.29
Xmas beads	14	0.33	0.530	1.92	2.53	0.28	1.46	0.13	0.30	0.16	0.026	0.15	0.013	0.032	0.005	0.025	0.005	7.89
Ink cartridge	15	<0.2	<0.02	<0.2	<0.02	<0.003	<0.02	<0.05	<0.003	<0.002	<0.003	<0.02	<0.003	<0.02	<0.005	<0.02	<0.003	<0.59
CD case (backing)	16	0.48	0.027	<0.2	0.050	0.015	0.040	<0.05	0.037	<0.002	<0.003	<0.02	<0.003	<0.02	<0.005	<0.02	<0.003	0.64
CD case (cover)	17	0.25	<0.02	0.24	<0.02	<0.003	<0.02	<0.05	<0.003	<0.002	<0.003	<0.02	<0.003	<0.02	<0.005	<0.02	<0.003	0.50
Desk corner cover	18	0.53	0.023	0.55	0.050	0.012	0.038	<0.05	0.006	<0.002	<0.003	<0.02	<0.003	<0.02	<0.005	<0.02	<0.003	1.21
Xmas candy container	19	0.60	<0.02	0.29	<0.02	0.005	<0.02	<0.05	<0.003	<0.002	<0.003	<0.02	<0.003	<0.02	<0.005	<0.02	<0.003	0.90
Bottle top	20	<0.2	0.038	<0.2	0.11	0.030	0.10	<0.05	<0.003	0.023	<0.003	<0.02	<0.003	<0.02	<0.005	<0.02	<0.003	0.30
Bottle top	21	<0.2	<0.02	<0.2	<0.02	<0.002	<0.02	<0.05	<0.003	<0.002	<0.003	<0.02	<0.003	<0.02	<0.005	<0.02	<0.003	<0.59
Take out container	22	<0.2	<0.02	0.65	<0.02	0.005	<0.02	<0.05	<0.003	<0.002	<0.003	<0.02	<0.003	<0.02	<0.005	<0.02	<0.003	0.66
Remote control	23	<0.2	<0.02	0.47	<0.02	<0.002	<0.02	<0.05	0.005	<0.002	<0.003	<0.02	<0.003	<0.02	<0.005	<0.02	<0.003	0.48
Water bottle	24	<0.2	<0.02	<0.2	<0.02	<0.003	<0.02	<0.05	<0.003	<0.002	<0.003	<0.02	<0.003	<0.02	<0.005	<0.02	<0.003	<0.59
Water bottle lid	25	<0.2	<0.02	<0.2	<0.02	<0.003	<0.02	<0.05	<0.003	<0.002	<0.003	<0.02	<0.003	<0.02	<0.005	<0.02	<0.003	<0.59
Yoghurt pot	26	<0.2	<0.02	<0.2	<0.02	<0.003	<0.02	<0.05	<0.003	<0.002	<0.003	<0.02	<0.003	<0.02	<0.005	<0.02	<0.003	<0.59
Bottle top	27	<0.2	<0.02	0.48	<0.02	0.004	<0.02	<0.05	<0.003	<0.002	<0.003	<0.02	<0.003	<0.02	<0.005	<0.02	<0.003	0.49
Fruit container	28	<0.2	<0.02	<0.2	<0.02	0.005	<0.02	<0.05	<0.003	<0.002	<0.003	<0.02	<0.003	<0.02	<0.005	<0.02	<0.003	0.005
Ink pen	29	0.37	<0.02	<0.2	<0.02	0.004	<0.02	<0.05	<0.003	<0.002	<0.003	<0.02	<0.003	<0.02	<0.005	<0.02	<0.003	0.37
Blackberry case	30	<0.2	<0.02	<0.2	<0.02	<0.003	<0.02	<0.05	<0.003	<0.002	<0.003	<0.02	<0.003	<0.02	<0.005	<0.02	<0.003	<0.59
Computer mouse	31	0.53	<0.02	<0.2	0.024	0.013	0.027	<0.05	<0.003	<0.002	<0.003	<0.02	<0.003	<0.02	<0.005	<0.02	<0.003	0.59

Tuner et al., Science of the Total Environment 774 (2021) 145405

How Monazite Forms in Nature?

- Monazite (REE phosphate) is known to exist below earth's surface in limited areas.
- Geologists report the formation of natural monazite requires extremely high pressures up to 25,660 atm (about 377,100 psi) and elevated temperatures.

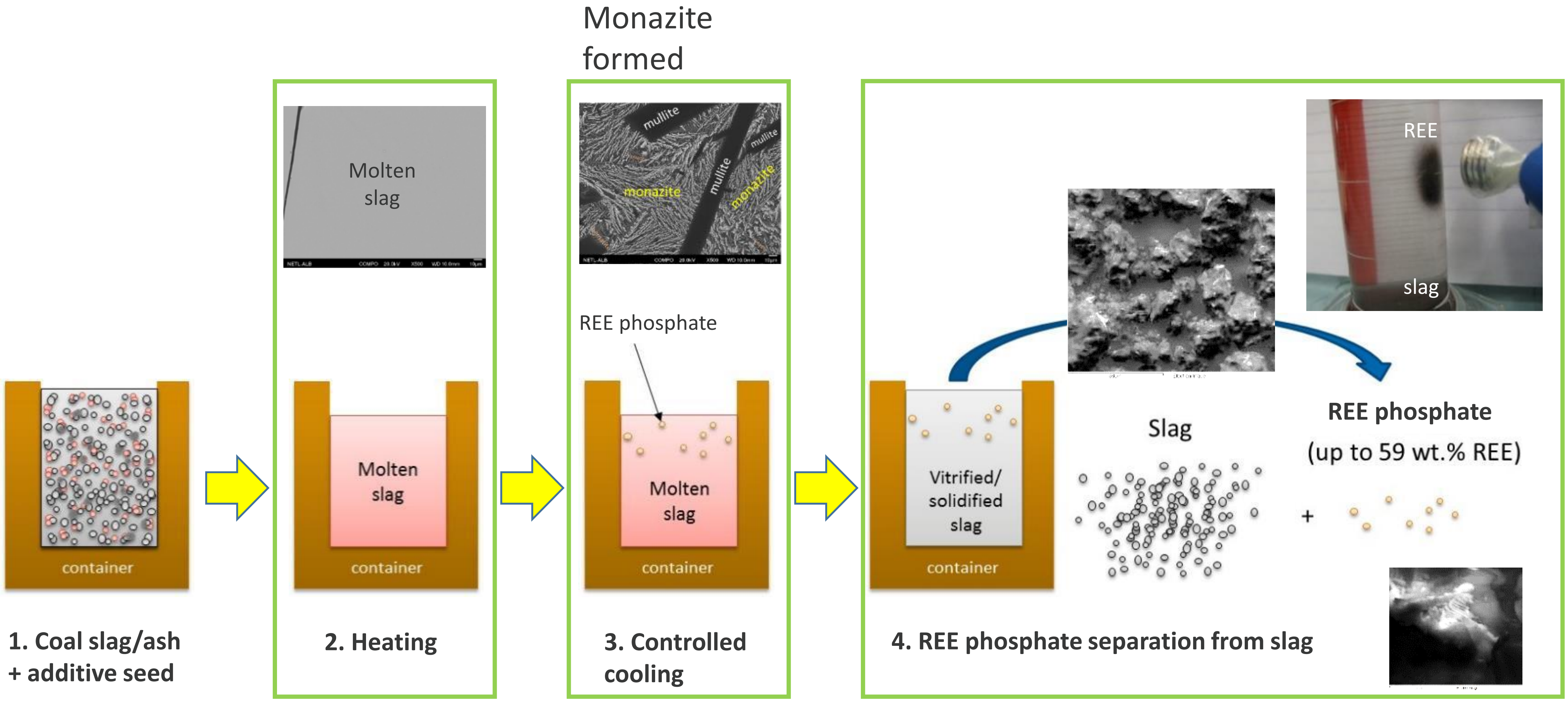
REE beneficiation technologies from monazite already exist.

Is it possible to **synthesize** monazite from recycling materials?

Molten 2021, Nakano et al.

NETL Thermal Fusion Approach

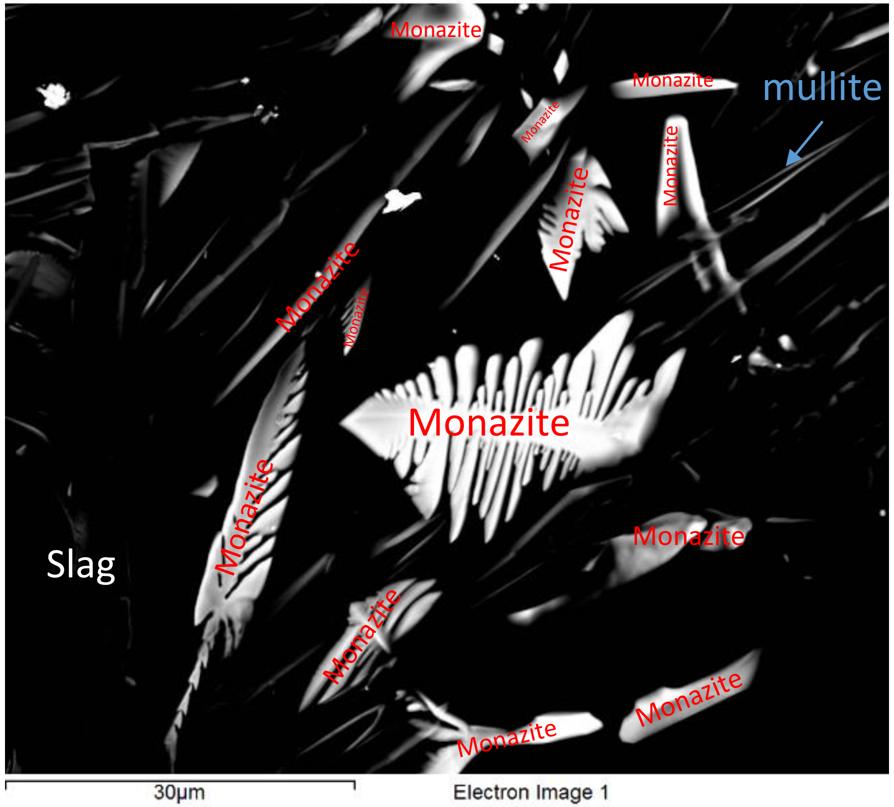
U.S. 10,358,694 B2 (Nakano, et al.)



Successful Monazite Formation in Air

NATIONAL ENERGY TECHNOLOGY LABORATORY

Synthetic coal slag (9% REE)



SEM-EDS (wt.%)

Phase	O	Al	Si	P	Ca	Fe	La	Sm	Ho
Mullite	54.9	32.1	9.8			3.1			
Monazite	28.0	0.6	0.5	12.2	0.4		18.2	17.1	23.0
Hematite	41.0	4.7	1.3	0.3	0.3	52.4			
Slag	69.8	7.2	15.8	1.9	2.8	2.4			0.1

Monazite

Element	Weight%
O	27.98
Al	0.57
Si	0.55
P	12.17
Ca	0.44
La	18.15
Sm	17.14
Ho	23.00

Light REE (La, Sm)

Heavy REE (Ho)

58.29 wt.%

(98.7 % purity)

LREEs and HREEs are both found in monazite, on the contrary to naturally occurring monazite.

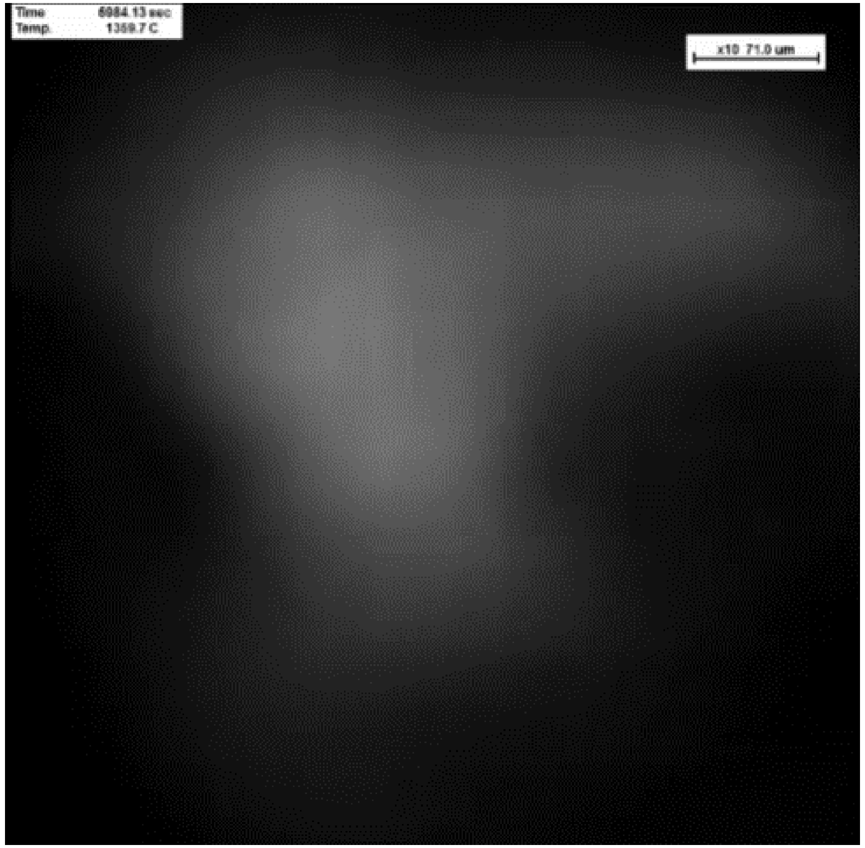
C.f. Theoretical max = 59 wt.%

Molten 2021, Nakano et al.

The Onset of Monazite Formation (CSLM)

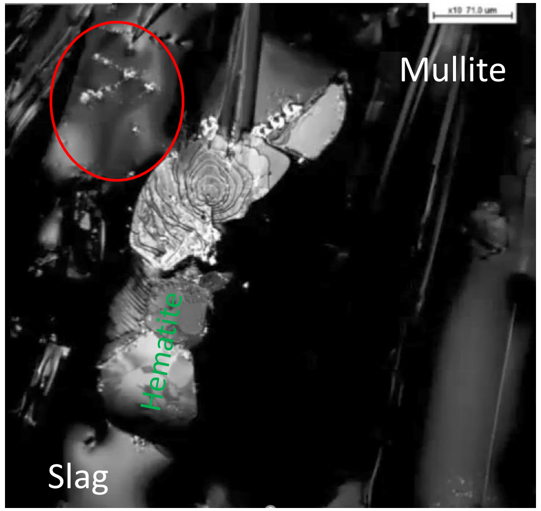
NATIONAL ENERGY TECHNOLOGY LABORATORY

Cooling from 1600 °C

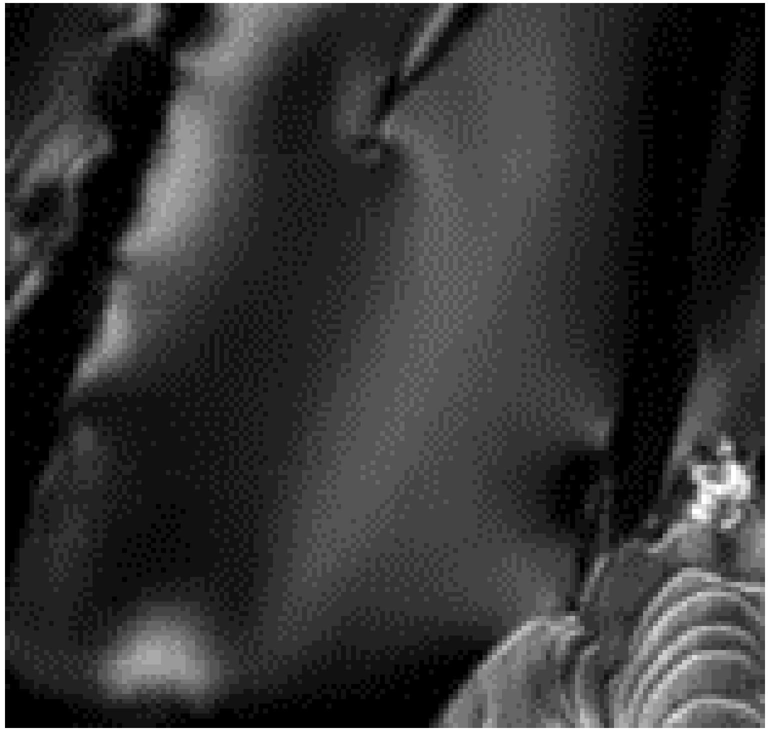


64x playback

Monazite



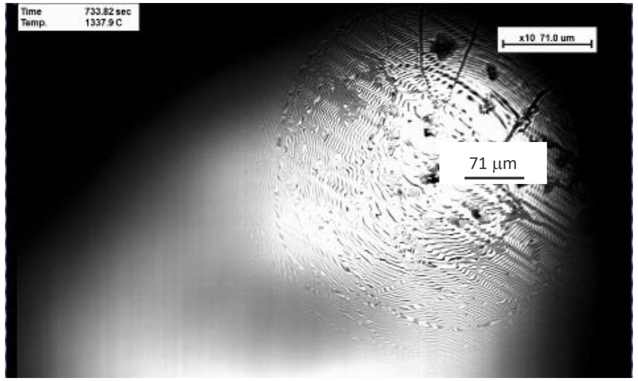
Close-up



64x playback

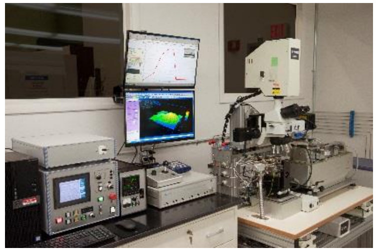
Nakano, et al., MOLTEN 2021

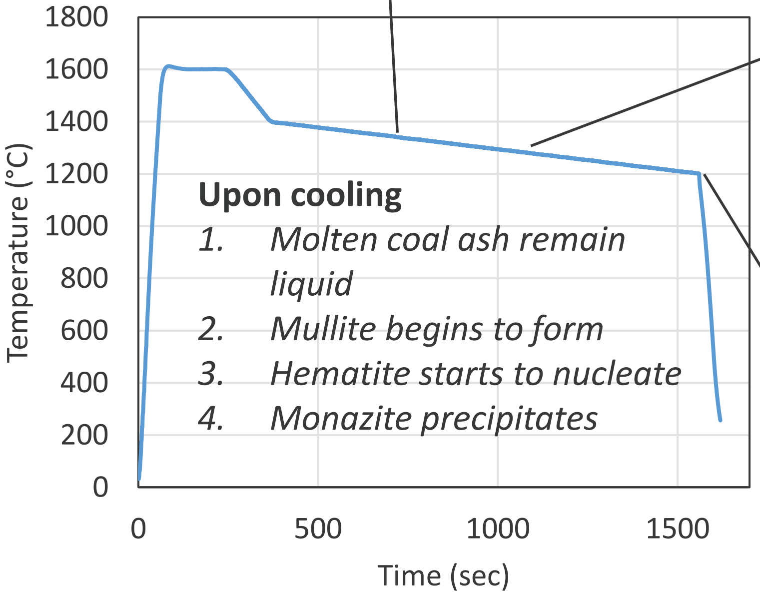
Phase Formation Temperatures (Tentative)

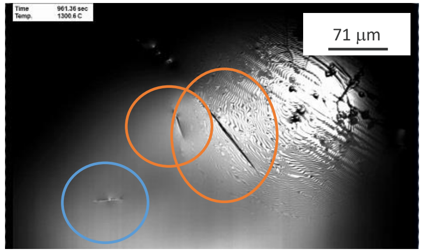


1) Molten coal ash

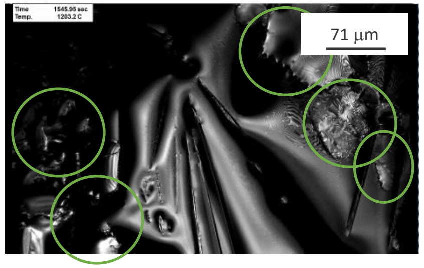
A confocal scanning laser microscope with a customized heating chamber was used to determine real time phase behaviors and monazite formation temperature in coal ash.





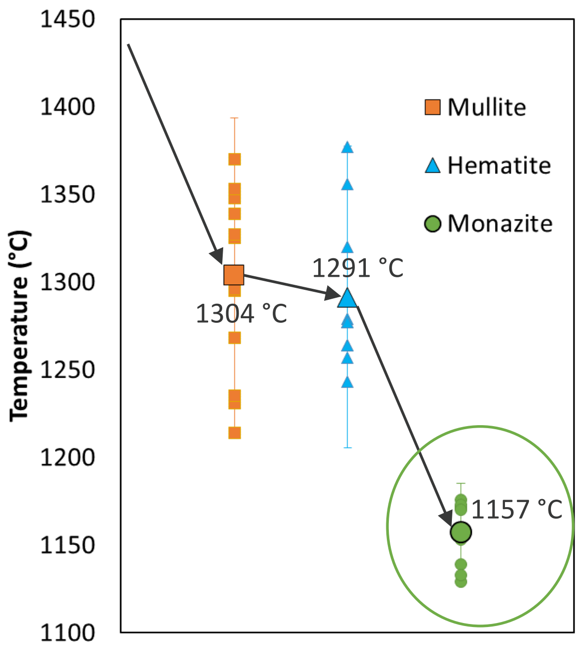


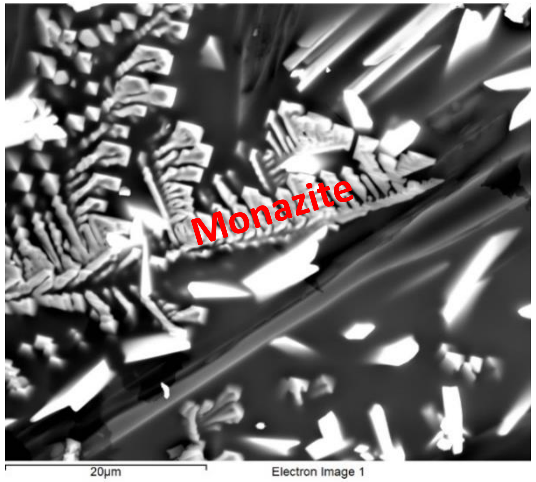
2) Mullite + Hematite forms



3) Monazite forms

Formation temperatures in slag on cooling (surface)





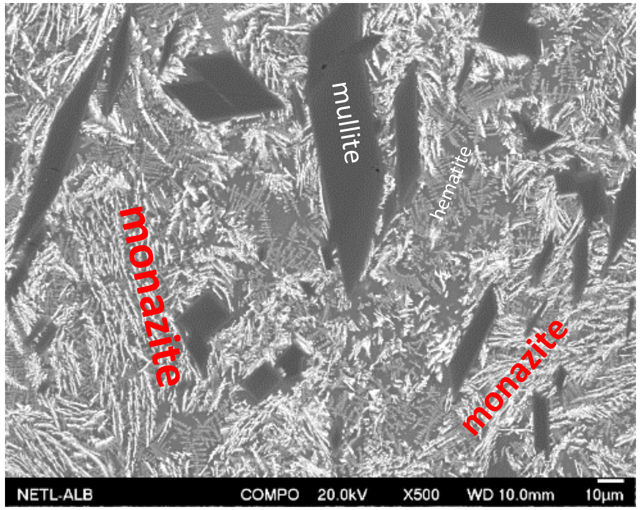
Monazite production by thermal approach

Empirical trials were performed to concentrate REEs into monazite ($REEPO_4$) from molten synthetic coal ash (slag) and cooling it under predetermined conditions. The monazite formation was successfully confirmed with coal ash containing down to 500 ppm REE. Concentration in monazite as high as **58 wt.% REE** was noted.

1. $P_2O_3^{4+}$ in slag ($P_2O_7^{4-}$ networking with O^{2-} similar to SiO_4^{4-})
2. $P_2O_3^{4+} + 2O^{2-} + REE^{3+} = REEPO_4$

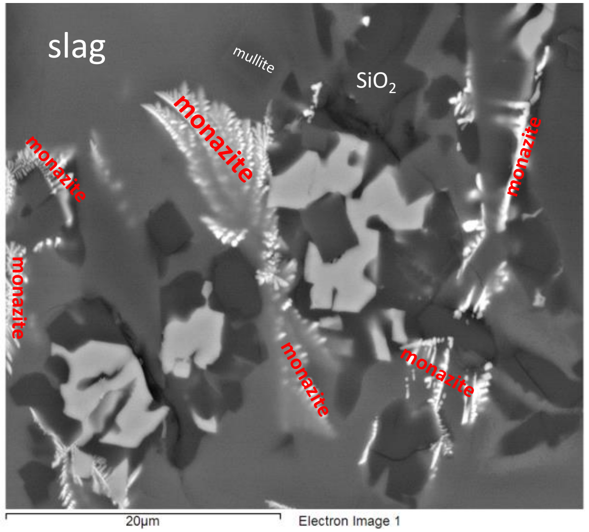
Coal ash with **9 wt.%** REE

Monazite



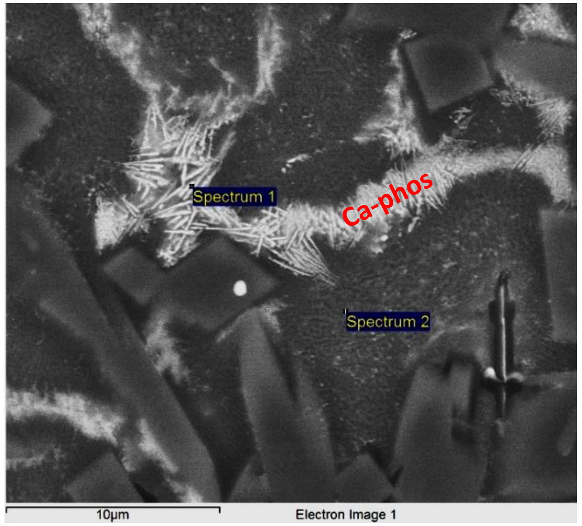
Coal ash with **3 wt.%** REE

Monazite



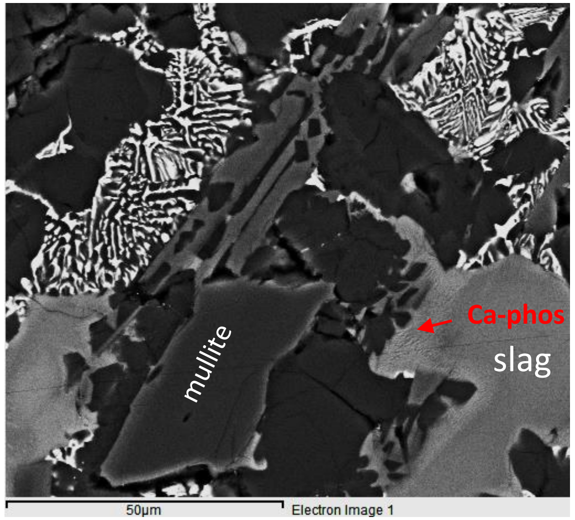
Coal ash with **0.1 wt.%** REE (**1000 ppm**)

Ca-phosphate



Coal ash with **0.05 wt.%** REE (**560 ppm**)

Ca-phosphate

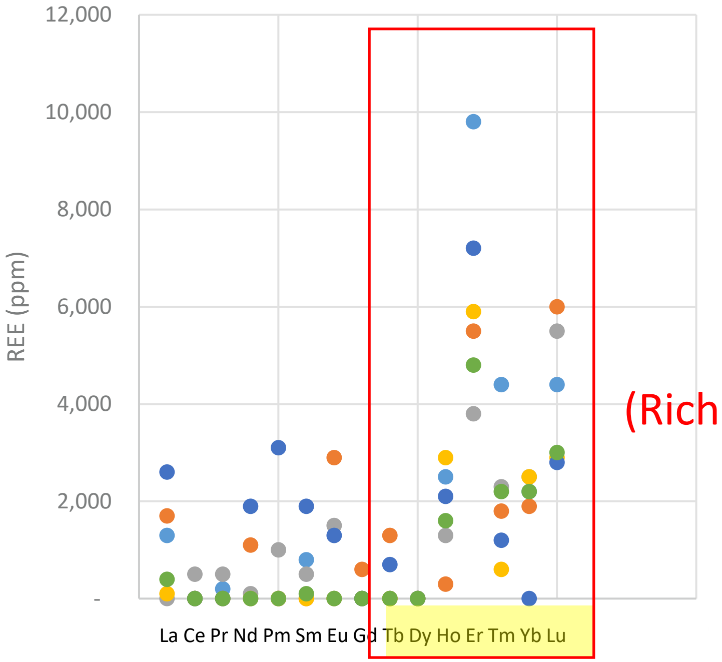


Scale-Up Demonstration: 3 kg Coal Ash

Industrial EAF

Fused ash

2.5% REE



(Rich in HREE)

- 0.058% REE in original ash
- 2.5% REE in the concentrate
- 83% REE yield
- HREE/LREEs : up to 148:1

- HREE: 1 – 15 ppm each in original ash
- Note Gd and Dy hidden behind Fe energy spectrum

Nickel and Vanadium

Ni, V from Petcoke By-Product

Compositions of industrial coal and petcoke ashes found in the U.S. and Canada.

(wt.%)	U.S. coal ash			U.S. petcoke ash			Canadian coal ash			Canadian petcoke ash		
Reference	[4]			[5,6]			[7,8]			[9,10]		
Ash components	Average	Min	Max	Average	Min	Max	Average	Min	Max	Average	Min	Max
SiO_2	43.6	7.1	68.5	13.6	1.6	23.6	52.0	35.5	67.3	41.4	37.0	50.1
Al_2O_3	25.1	4.1	38.6	5.6	0.5	9.4	18.6	16.3	20.3	19.6	14.4	24.9
TiO_2	0.6	0.0	3.7	0.2	0.0	0.4	0.7	0.5	0.8	2.3	0.6	4.8
Fe_2O_3	17.0	2.1	69.7	9.3	2.5	31.6	9.4	2.6	32.0	9.9	7.4	12.1
CaO	5.8	0.5	45.1	5.4	2.2	11.9	6.9	2.3	13.6	5.1	1.6	15.8
MgO	1.2	0.0	8.0	1.2	0.2	5.1	1.4	0.9	2.7	1.9	1.3	3.9
Na_2O	0.3	0.0	6.5	0.7	0.1	1.8	1.9	0.4	6.0	1.2	0.7	1.7
K_2O	0.4	0.0	3.5	0.6	0.3	1.2	1.4	0.3	2.3	1.6	0.9	1.9
SO_3	4.1	0.0	32.3	3.8	0.8	13.8	4.5	1.1	14.3	2.6	1.9	7.1
P_2O_5	0.1	0.0	8.0	–	–	–	0.2	0.0	0.6	0.1	0.0	0.4
NiO	–	–	–	8.8	2.9	12.0	0.0	0.0	0.0	1.9	1.1	2.6
V_2O_5	–	–	–	49.4	19.7	74.5	0.0	0.0	0.0	10.1	3.2	20.3
Total	98.3			98.6			97.1			97.8		
SiO_2/Al_2O_3	1.73			2.45			2.79			2.11		

J. Nakano et al./Fuel 161 (2015) 364–375

Saudi

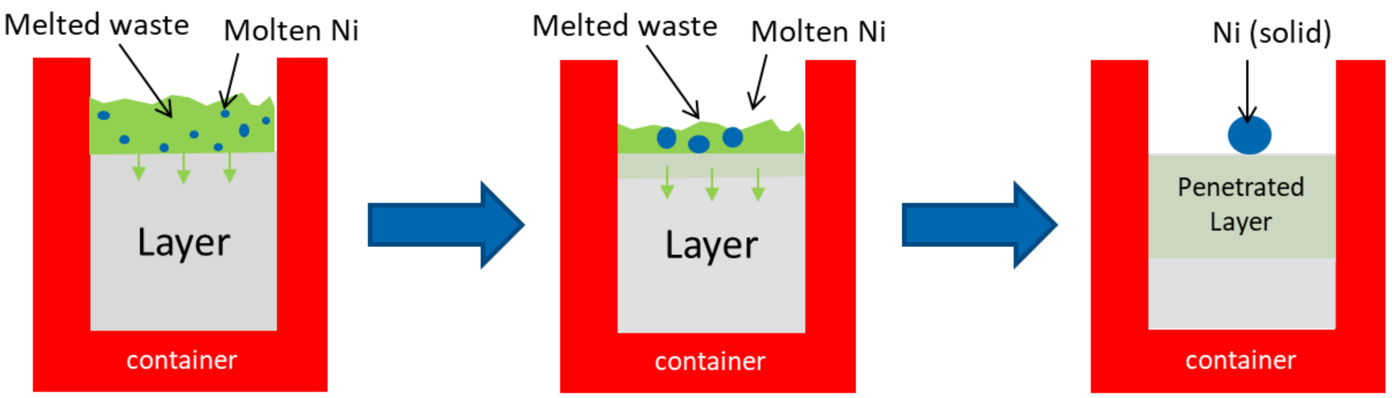
(wt%)	
Arsenic (As)	0.044
Cadmium (Cd)	0.065
Cobalt (Co)	0.065
Chromium (Cr)	0.080
Copper(Cu)	3.370
Mercury (Hg)	0.005
Nickel (Ni)	**34.848**
Lead (Pb)	0.217
Selenium (Se)	0.229
Vanadium (V)	**58.489**
Zinc (Zn)	2.587
total	100.000

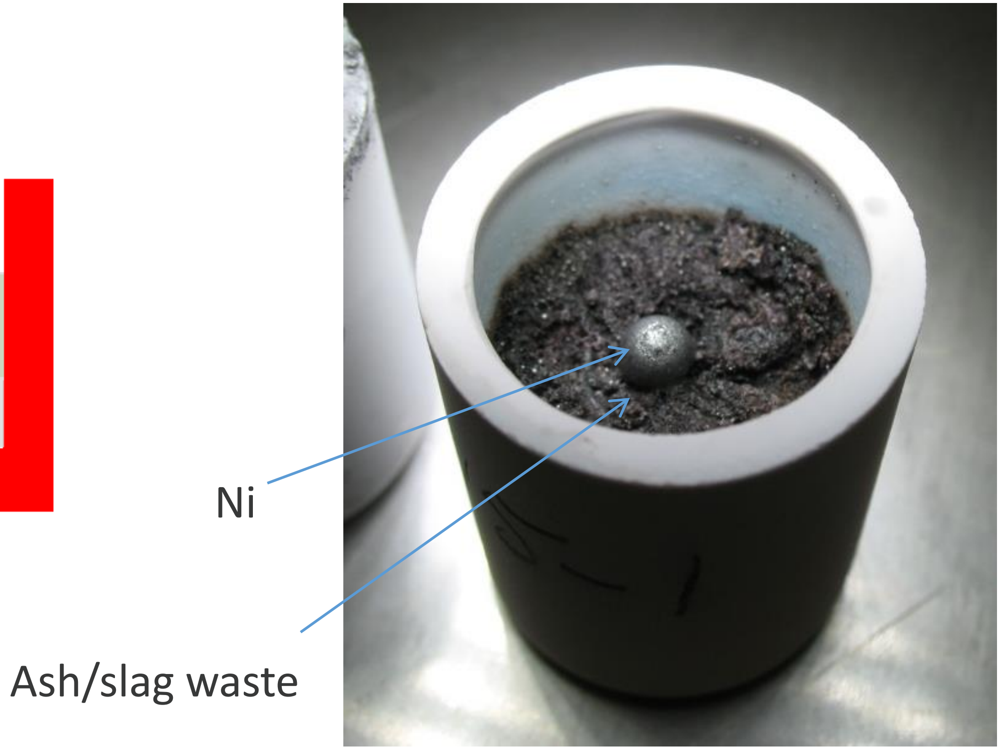
Int. J. Environ. Sci. Technol. (2014), A. Mofarrah, et al.

Ni, V from Petcoke By-Product

U.S. 10,323,298 B2 (Nakano, et al.)

NETL carbothermal technology





Ni, V from Petcoke By-Product

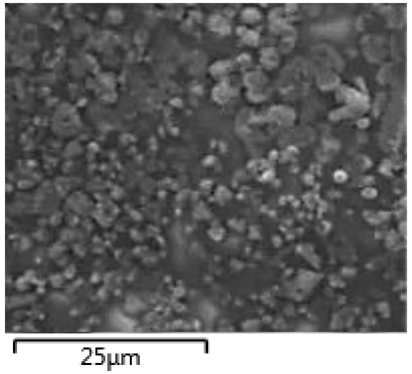
Petcoke slag from gasification power plant

(wt.%)	Na	Mg	Al	Si	P	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Zr	Mo	REE (total)
Petcoke slag	2.7	1.0	14.8	47.4	0.7	2.1	5.1	0.008	0.9	6.7	0.1	0.08	13.9	2.7	1.3	0.03	0.09	0.03	0.01	0.08	0.007	0.03	0.08	0.0455

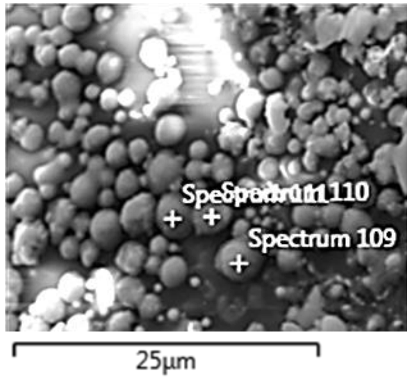
NETL Thermal technology

Embodiment 1
(Carbothermal)

Vanadium oxide
(30% V)



Ferronickel
(60-75% Ni)

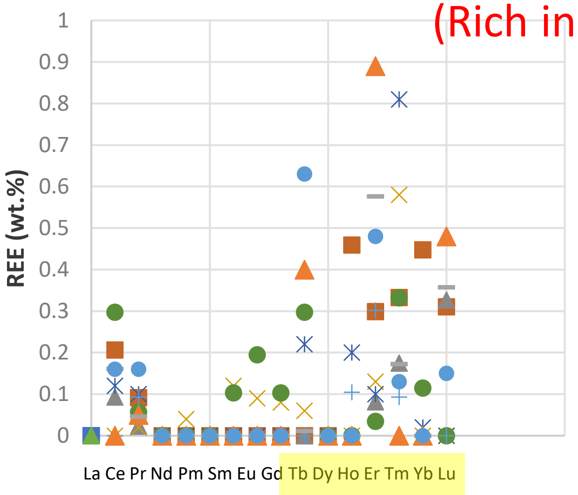


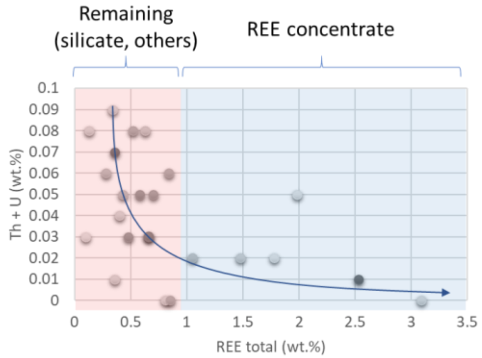
Embodiment 2
(Non-carbon)

3% REE

REE in the concentrate

(Rich in HREE)

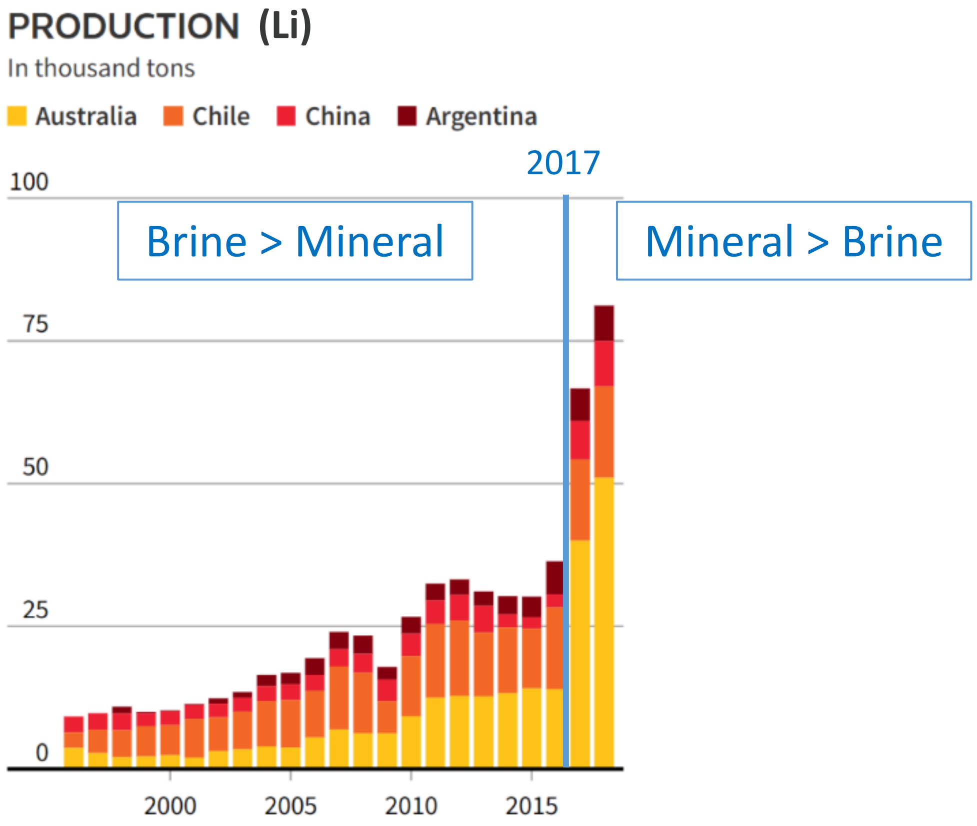




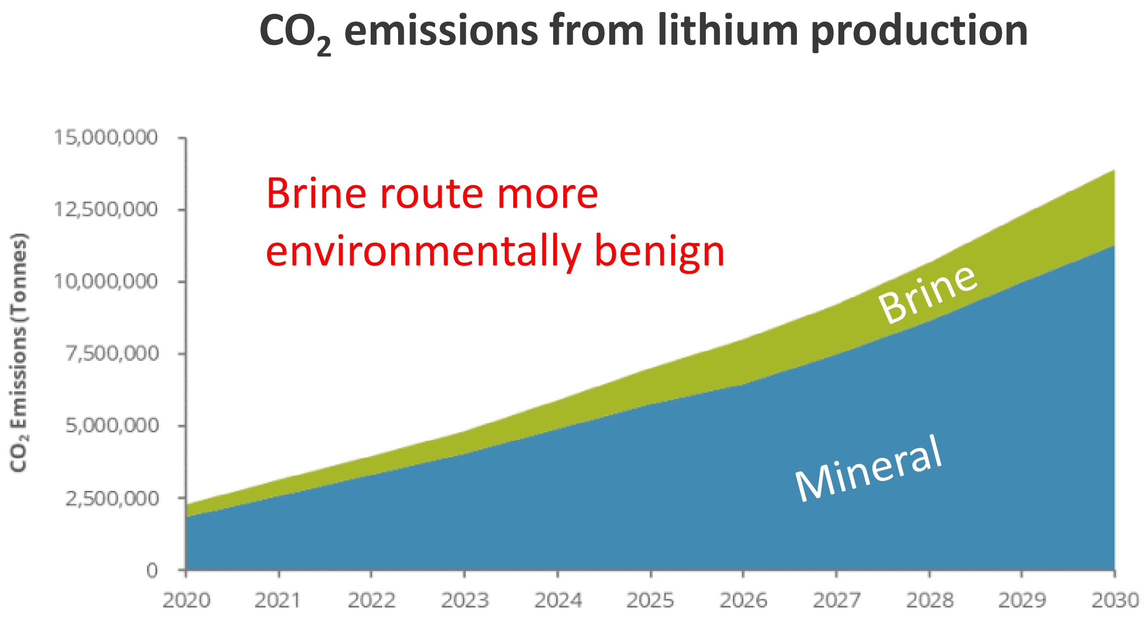
- HREE: 0.0001 – 0.0015 % each in original slag
- Gd and Dy hidden behind Fe energy spectrum

Lithium

Technological Need for Brine Sources

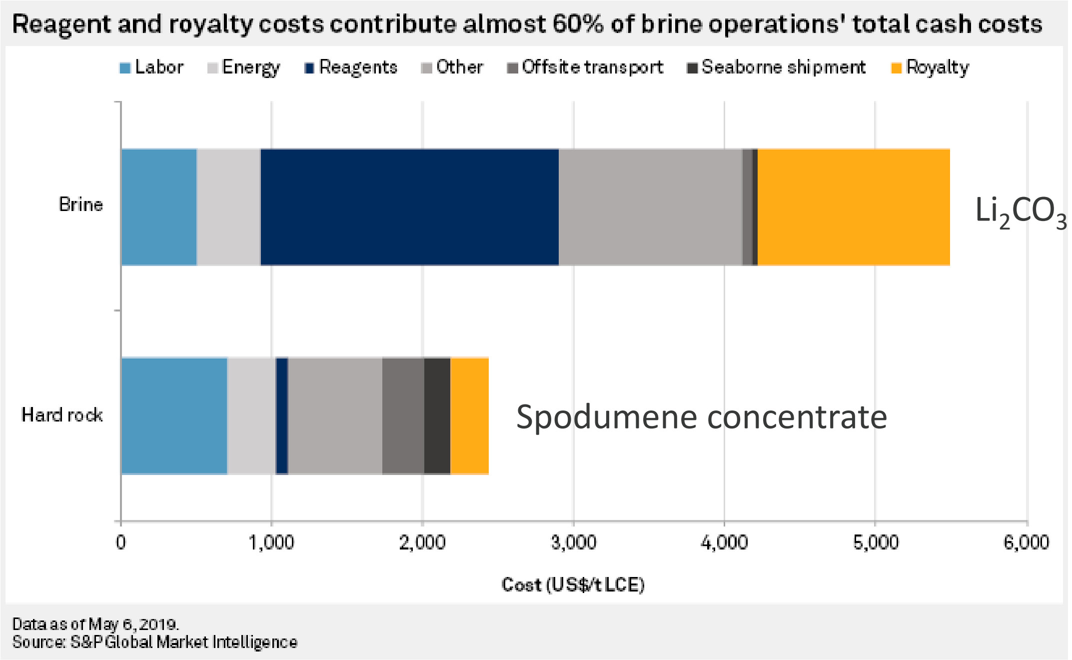


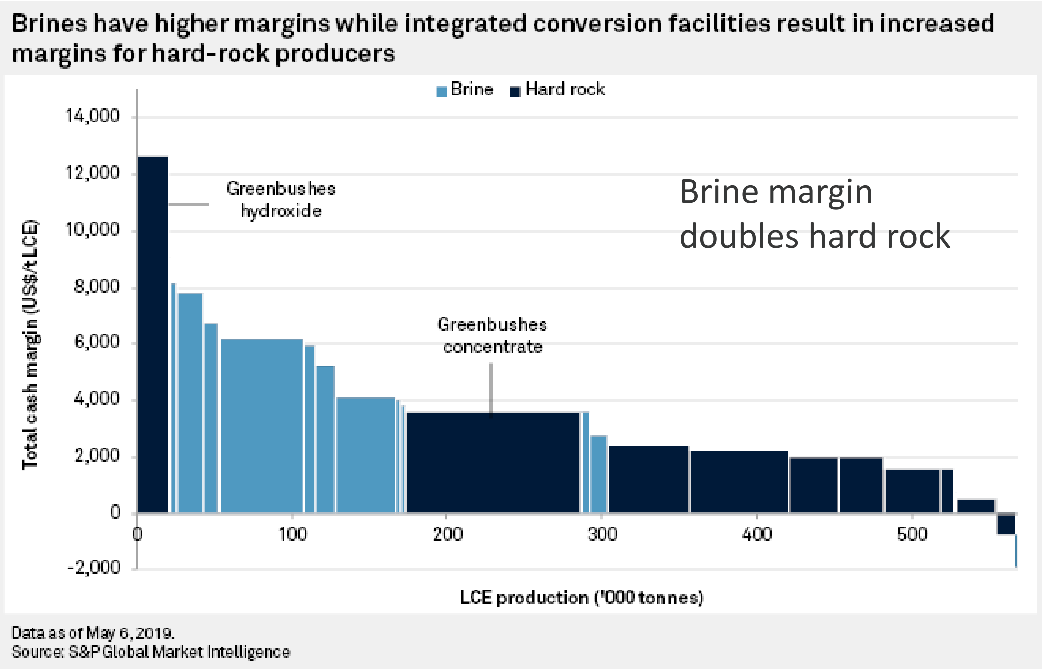
Reuters-environment, 2019



Green Car Congress, Oct 6, 2020

Economics

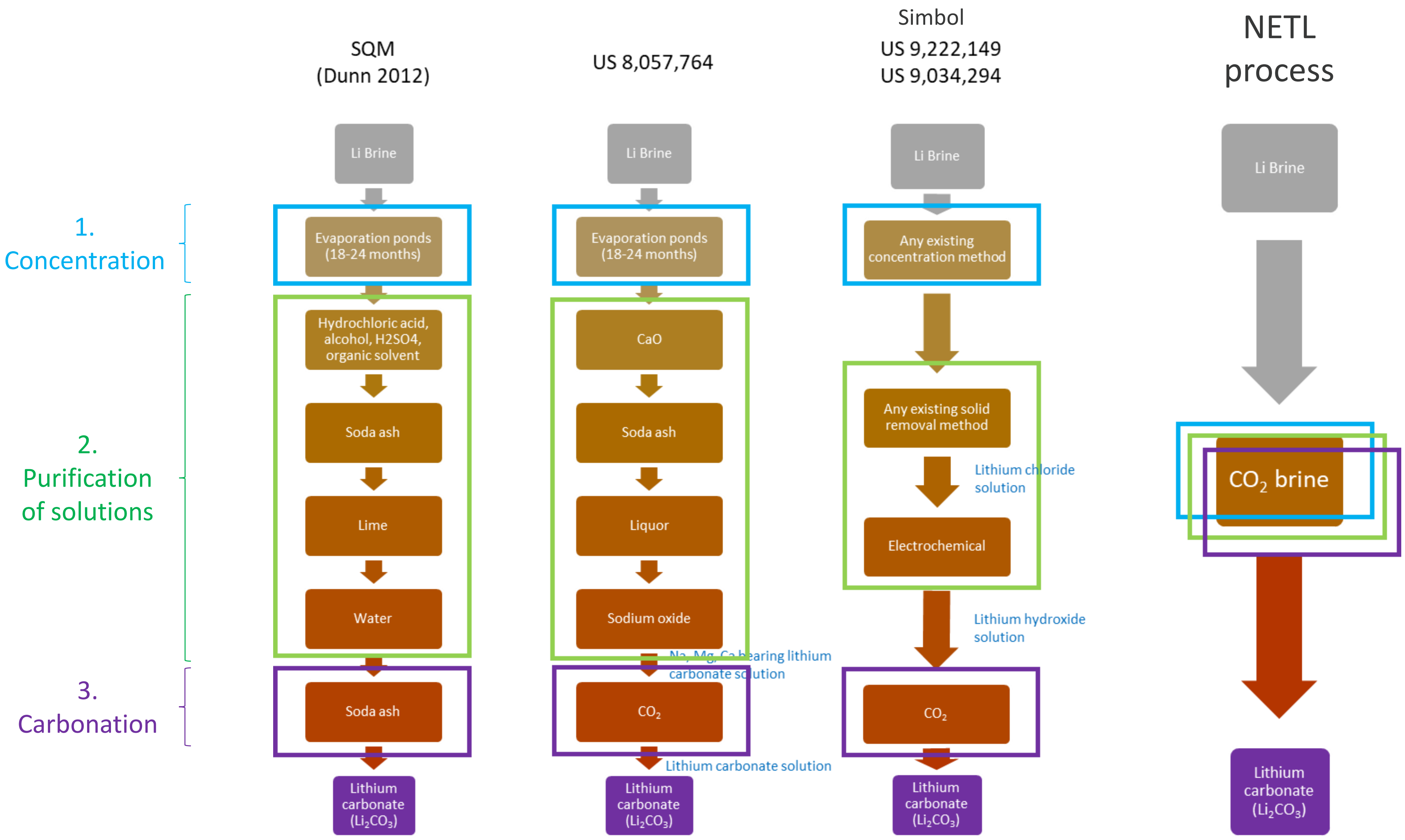




Li prices (as of 2019):

- Spodumene concentrate: $4,587/t
- Li_2CO_3: $12,500/t

Existing Brine Processes

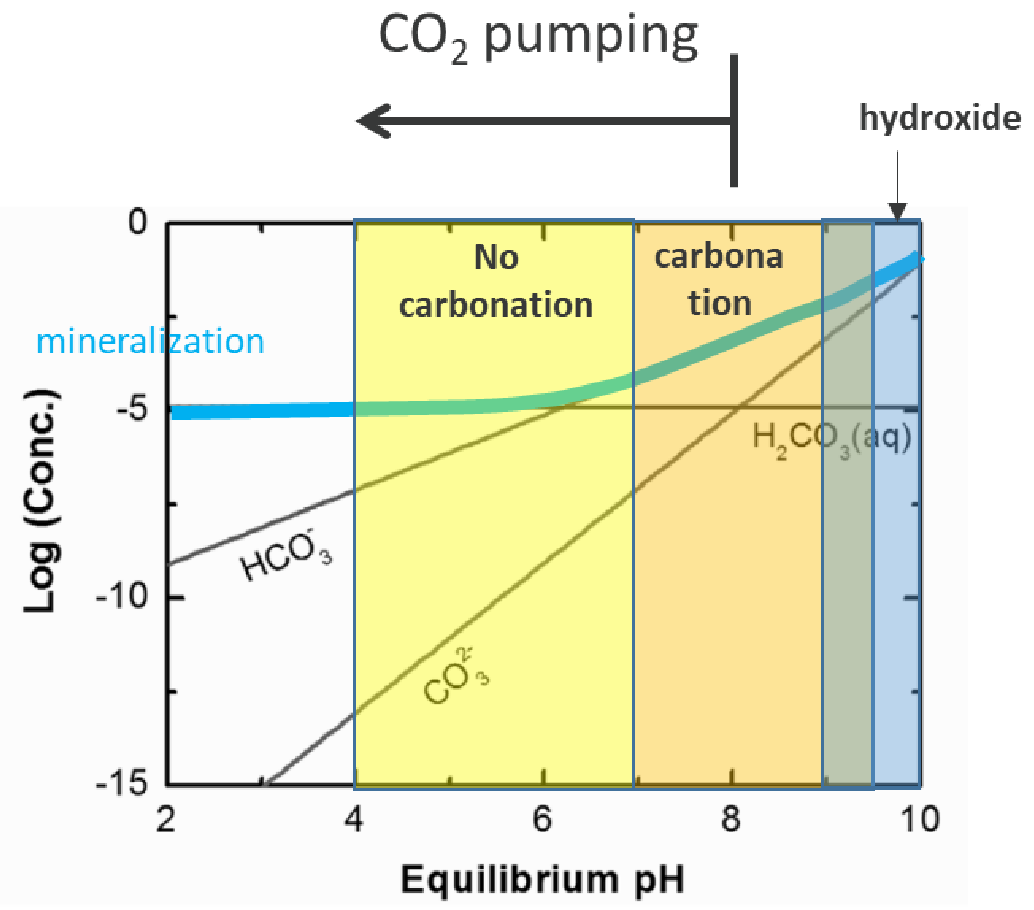


Challenges with CO_2 Pumping Approach

- ***CO_2 pumping*** is one of the known techniques to cause ***mineralization*** with elements dissolved in liquids such as sea water and brine:

$$CO_2 + H_2O + 2Li^+ = 2H^+ + Li_2CO_3$$

- However, as ***more CO_2*** is pumped in, it acidifies the liquid, which ***reverses the reaction***, limiting outcome.
- This ***dilemma*** has never been solved in industry without modifying the system: Thermodynamic manipulations.



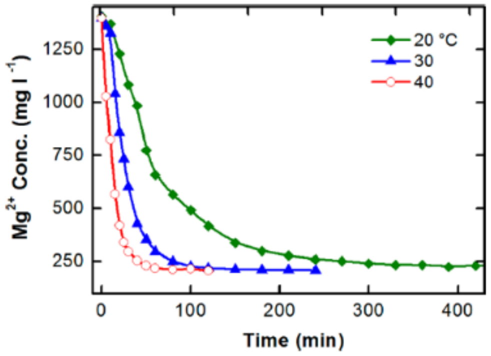
Modified from: Ma, energy and fuels, 2013, 27, 4190-4198

Existing CO_2-Based Extraction Techniques

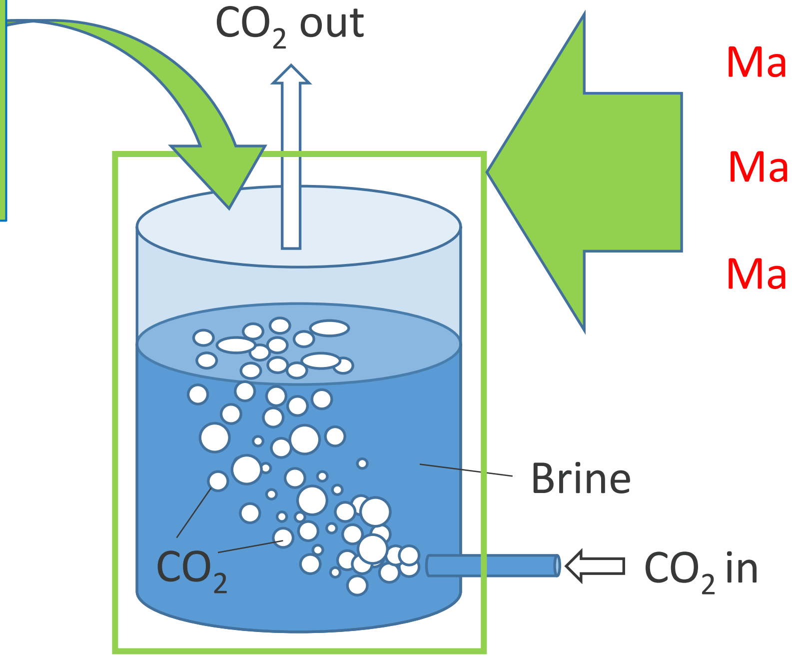
(Thermodynamic manipulations)

Manipulation 1

Alkali chemicals must be added to adjust the pH (NaOH, soda, forsterite, limestone).
c.f., up to 5 times CO_2 mass required to raise the pH to 6.8.[1]



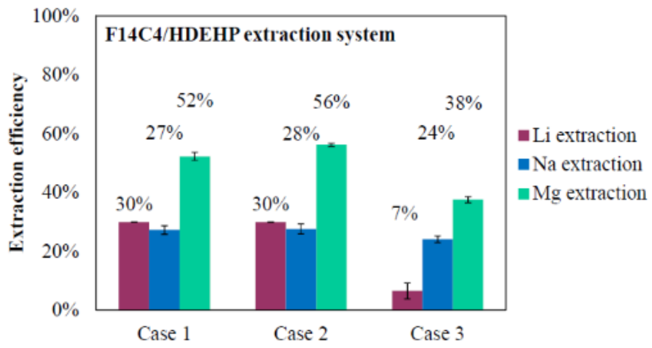
2013 Ma et al.



Manipulation 2 — Apply pressure

Manipulation 3 — Apply heat

Manipulation 4 — Supercritical



2019 Pálsdóttir

Manipulation 5 — Any other parameters

Manipulation 6 — Combination thereof

Low pH maintained throughout injection (low carbonation)

NETL's Previous Approach: Supercritical CO_2

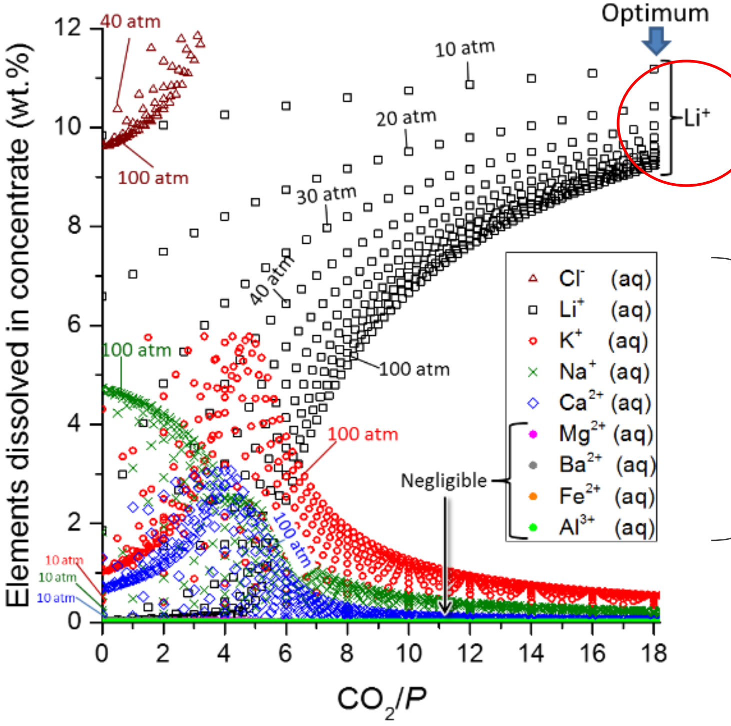
NATIONAL ENERGY TECHNOLOGY LABORATORY

U.S. 10,315,926 B2 (Nakano, et al.)

16/537,985 (Nakano, et al.)

Brine + CO_2

Vessel 1 (Concentration)



Undesired solid precipitates

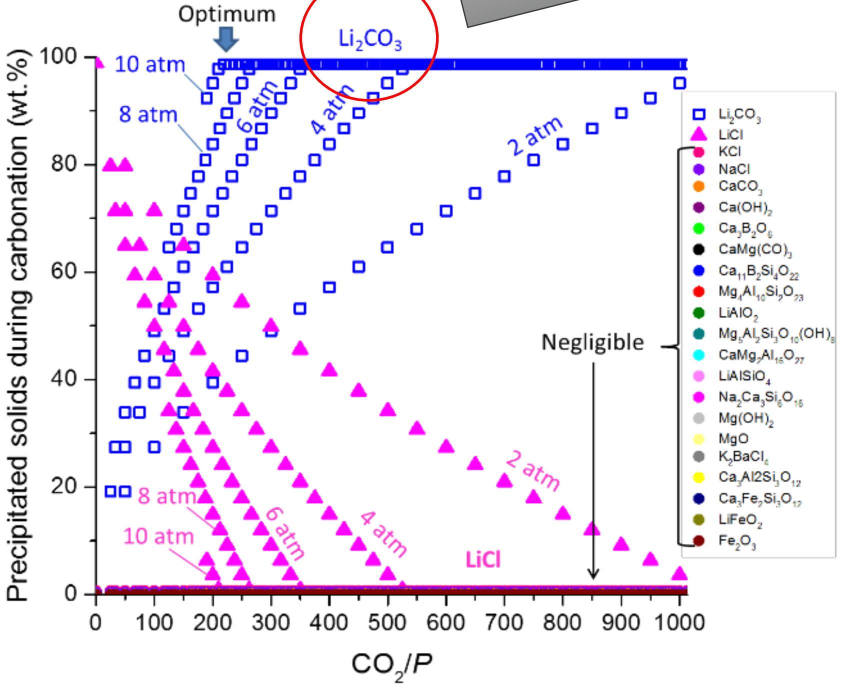
LiCl solution

Vessel 2 (Carbonation)

Only Li_2CO_3 precipitates out as solid particles

product

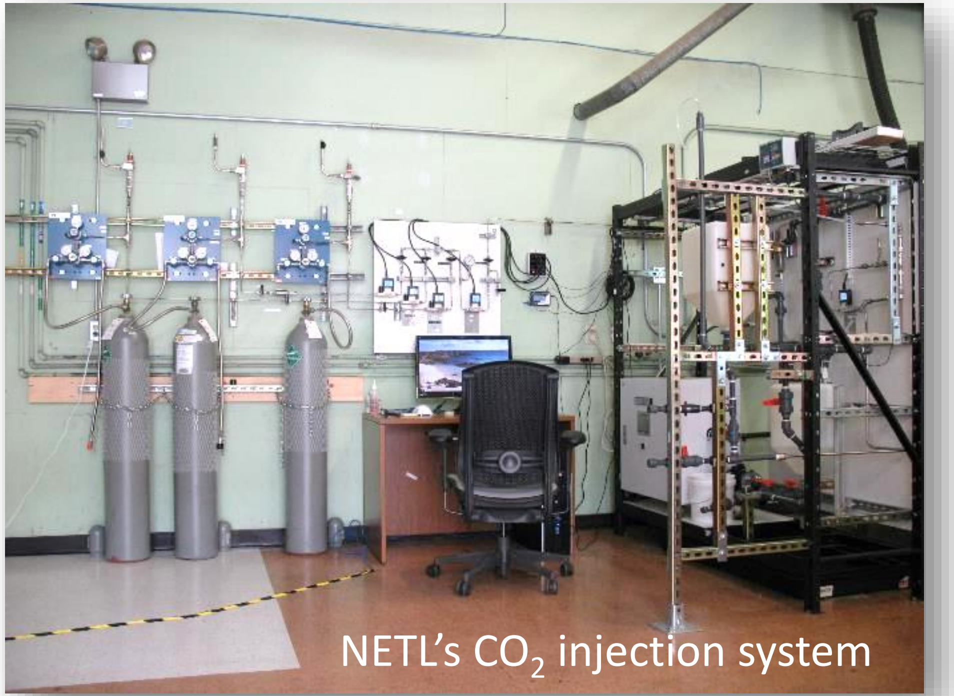
Li_2CO_3



Undesired species remain in brine.

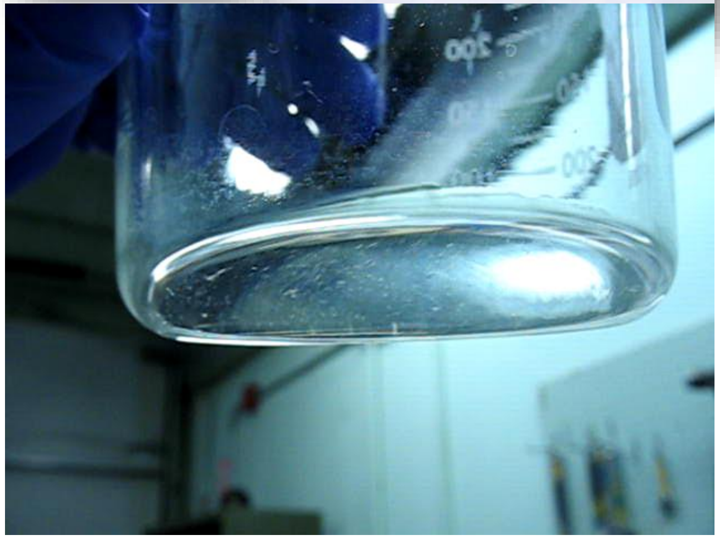
NETL's Current Approach: 'Ambient' CO_2 Injection

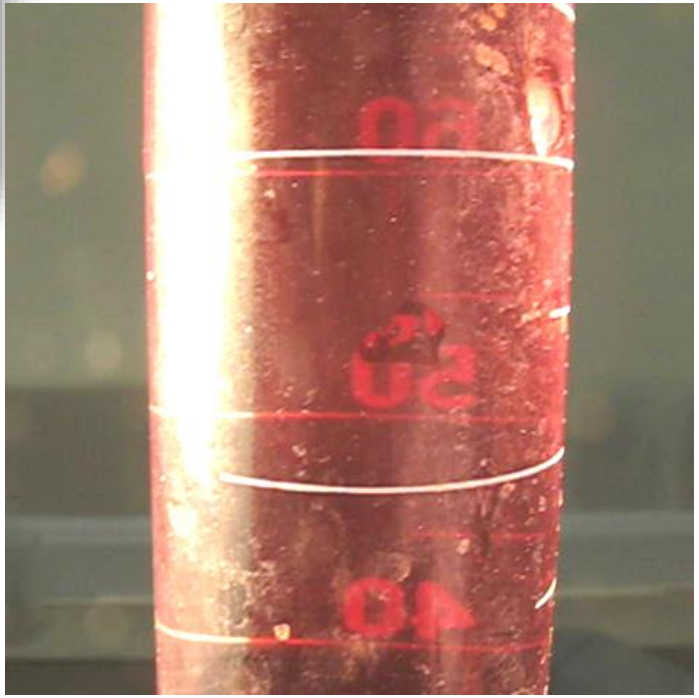
Designed and developed for Li recovery from brines



NETL's CO_2 injection system

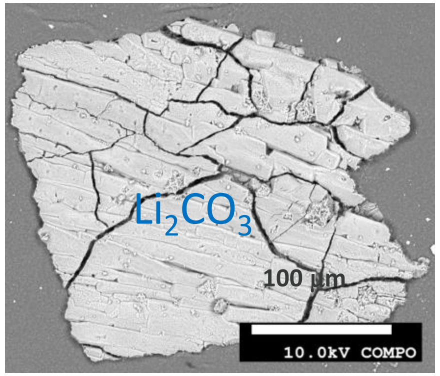
Controlled CO_2 can be injected into a brine in a continuous fashion (up to 1,500 L/hr).





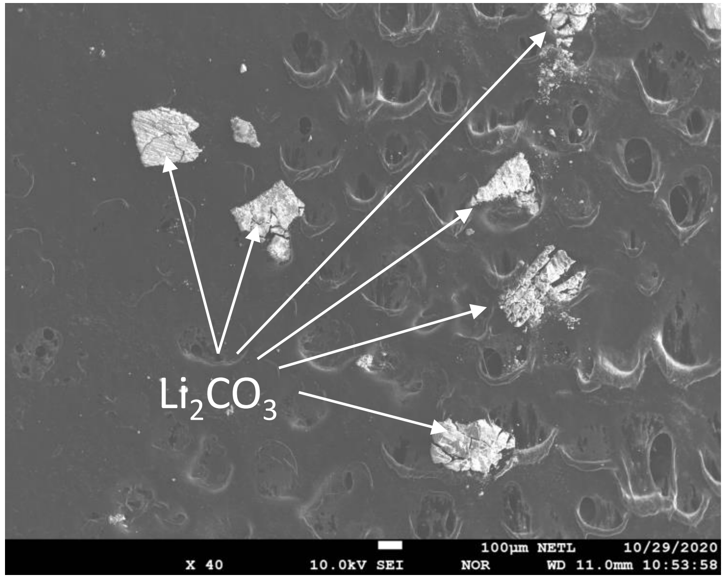
Product: High Purity Li_2CO_3

Dissolved solids: Li (0.3%), Ca, Si, Cu, Fe, Na, Cl

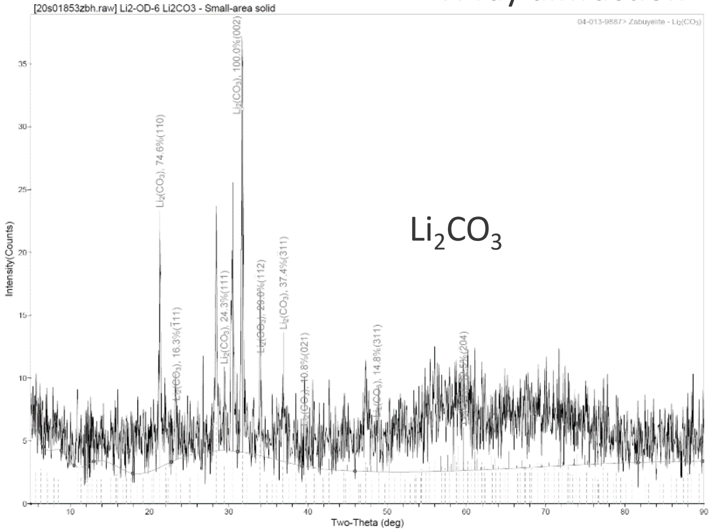


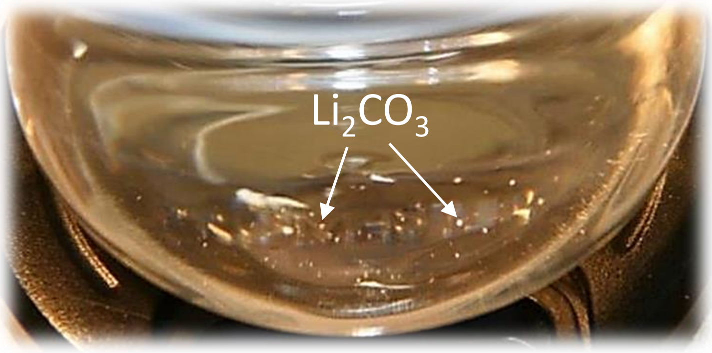
> 99.8 % purity

Formula	mass%	Atom%
C	18.77	23.57
O	80.80	76.17
Na	0.31	0.20
Si*	0.08	0.04
Cu*	0.04	0.01
Total	100.00	100.00



X-ray diffraction





Lithium Carbonate Kinetics

NETL's current approach: Ambient CO_2 injection

Li water (fresh)

Dissolved solids: Li (0.3%), Ca, Si, Cu, Fe, Na, Cl

Li brine (saline)

Dissolved solids: Li (0.3%), Ca, Si, Cu, Fe, NaCl (8%)

No salt precipitates

Current Status

- Verified with 3,000, 300, and 30 ppm Li (i.e., 0.3, 0.03, and 0.003 % Li)
- Validated with oil & gas produced brine with 18 ppm Li (0.0018 % Li)
- 2 license applications submitted to NETL
- 2 CRADAs in process
- Encouraging diversified use of field

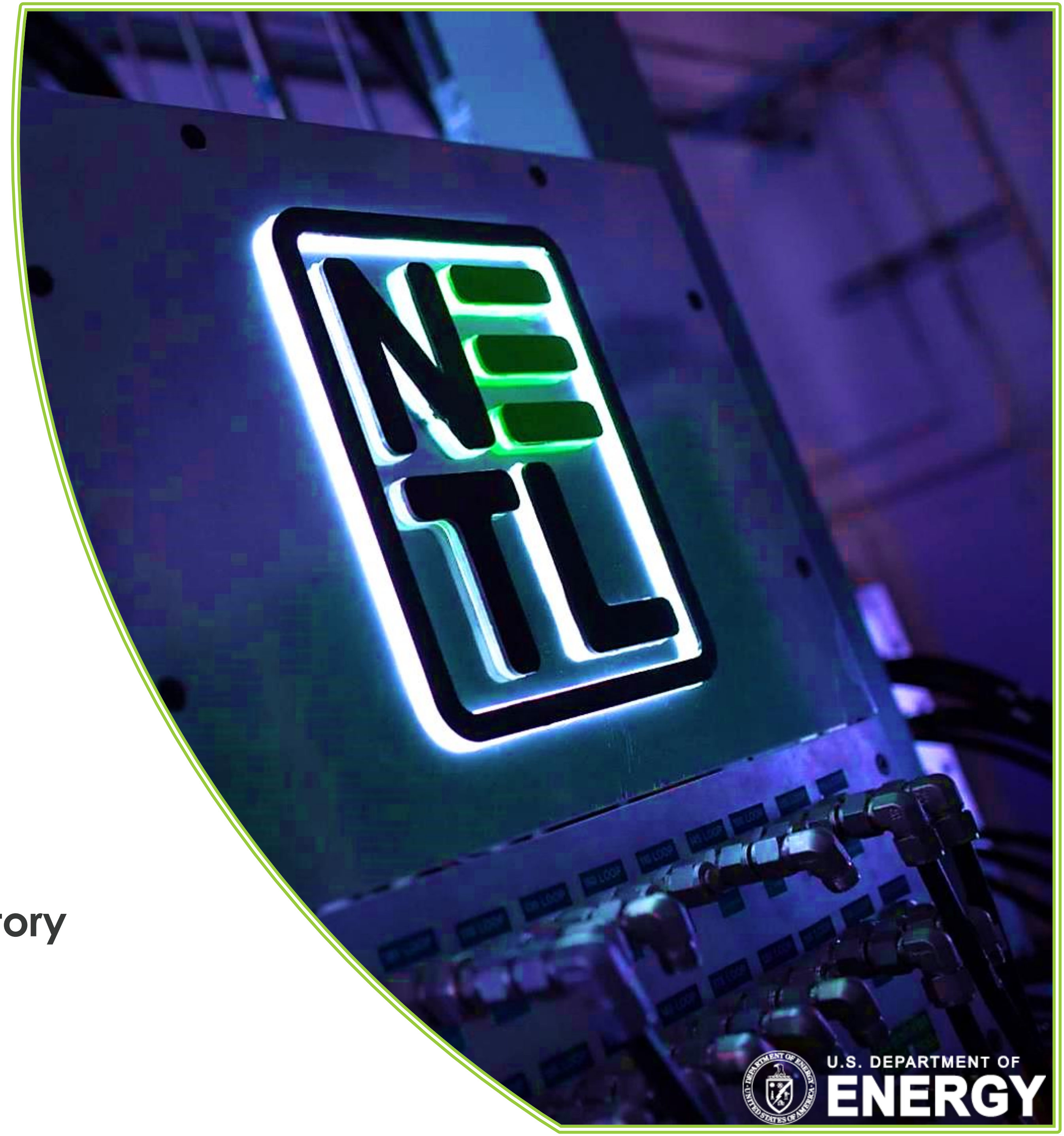
NETL Resources

VISIT US AT: **www.NETL.DOE.gov**

@NETL_DOE

@NETL_DOE

@NationalEnergyTechnologyLaboratory



NETL
CONTACTS

Presenter: Jinichiro Nakano
(jinichiro.nakano@NETL.DOE.gov)

Technology Transfer: Jessica Lamps
(jessica.lamp@NETL.DOE.gov)

Federal supervisor: Marisa Arnold
(marisa.arnold@NETL.DOE.gov)

Associate director: David Alman
(david.alman@NETL.DOE.gov)