UNCLE-SAM- Developing biomining applications of seaweeds for sustainable, domestic production of critical REE mineral feedstocks

(***U***nrealized ***C***ritical ***L***anthanide ***E***xtraction via ***S***ea ***A***lgae ***M***ining)

OR

Seaweeds for Cellphones

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Seagriculture

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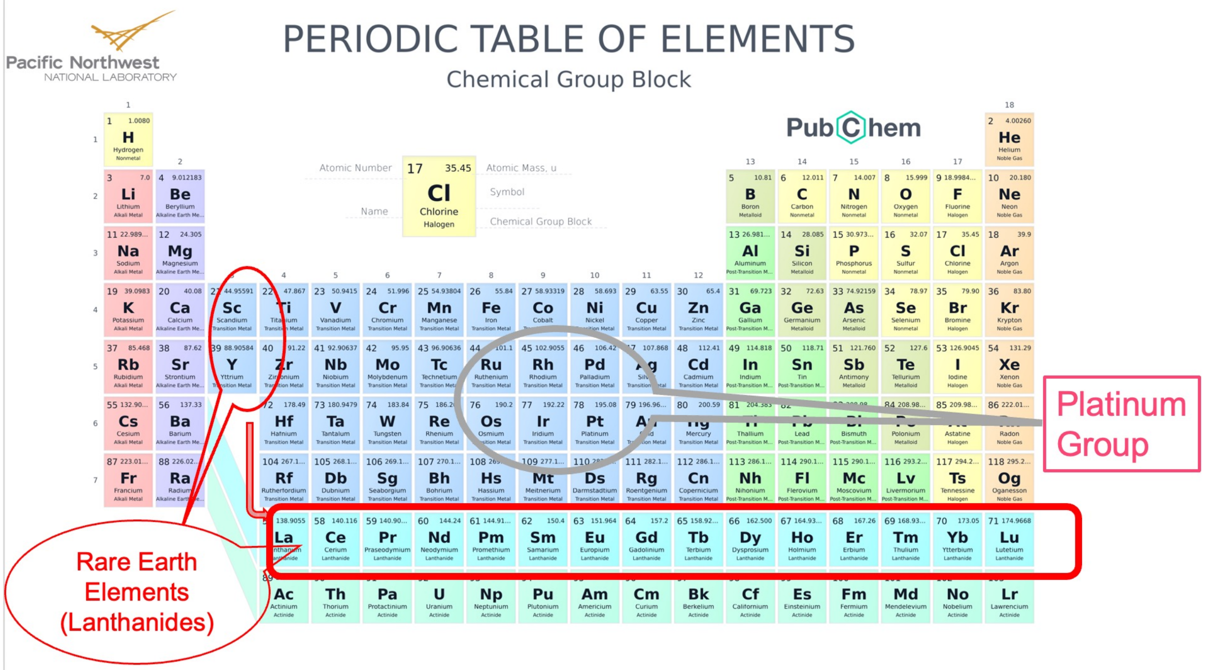
Rare Earth Elements (Lanthanides)



Critical in making:

- Batteries → EV,s
- Magnets
- Alloys
- Lasers
- Phosphors
- Glass
- PET Scan detectors
- Fuel Cells
- Catalytic converters
- Etc….

Technology White Space Addressed

Current state of technology

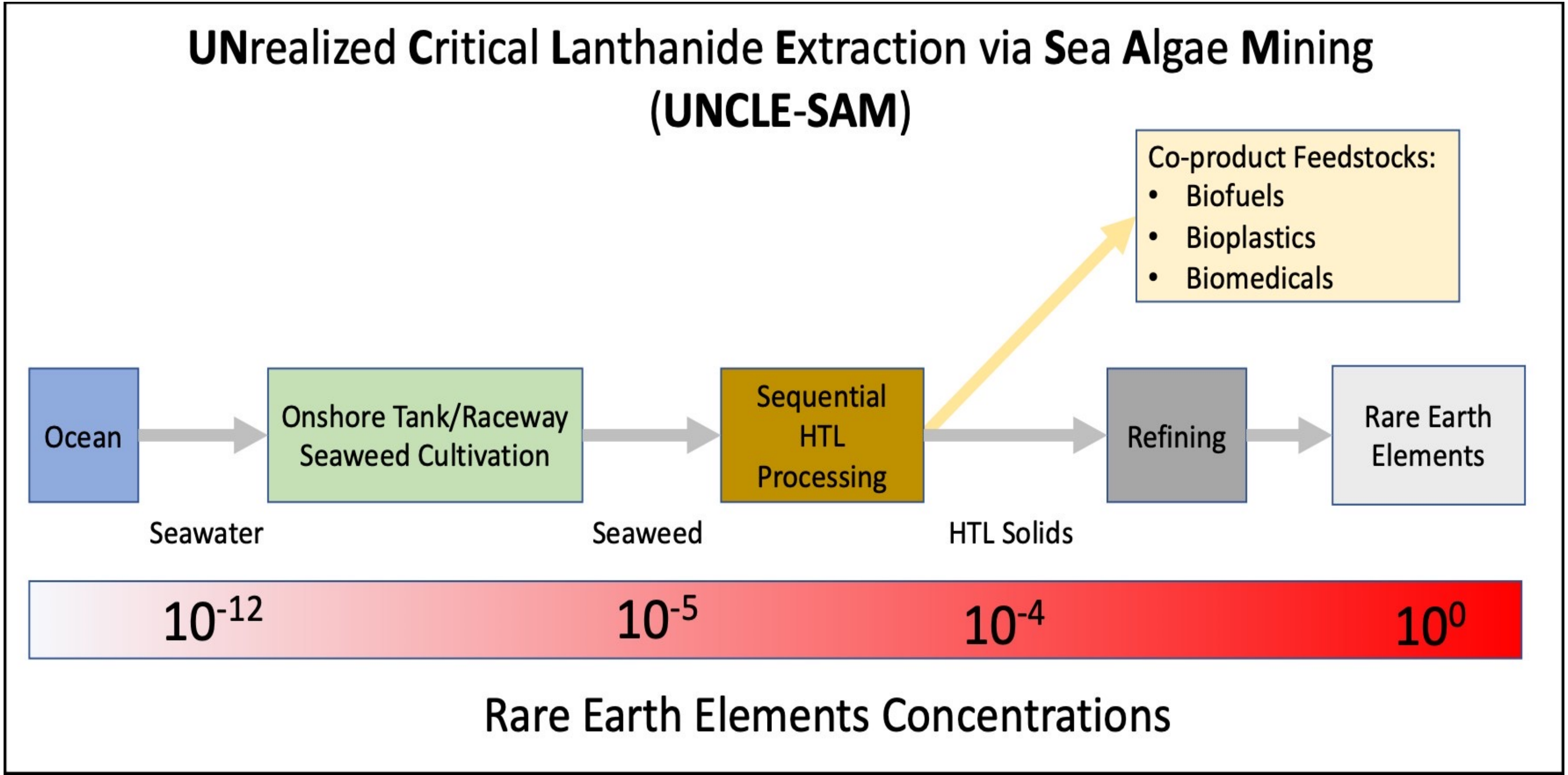
- Current processes for rare earth elements (REE) extraction from terrestrial ores are:
  - Energy Intensive
    - Excavation
    - Crushing/Grinding
  - Environmentally Damaging
    - Habitat destruction
    - Surface and ground water impacts
  - Have limited economically viable deposits
  - Are geopolitically sensitive
    - US is import-reliant on many REEs

Key challenge with tech approach

- The Ocean represents one of the single largest REE reservoirs on Earth, however the dissolved concentrations are extremely dilute and have been considered too energy intensive to concentrate for practical applications.
- Bioconcentration of Critical Minerals via **Sea Algae Mining** may provide a paradigm shift for sustainable ocean mining.

Pacific Ocean, photo credit: ISS007-E-07304

Conceptual UNCLE-SAM Process



UNrealized **C**ritical **L**anthanide **E**xtraction via **S**ea **A**lgae **M**ining

(**UNCLE-SAM**)

Co-product Feedstocks:
- Biofuels
- Bioplastics
- Biomedicals

Ocean

Onshore Tank/Raceway Seaweed Cultivation

Sequential HTL Processing

Refining

Rare Earth Elements

Seawater

Seaweed

HTL Solids

10^{-12} 10^{-5} 10^{-4} 10^{0}

Rare Earth Elements Concentrations

Bioconcentration factor of Seaweeds from the Salish Sea (ash basis).

REE Bioconcentration benchmark achieved

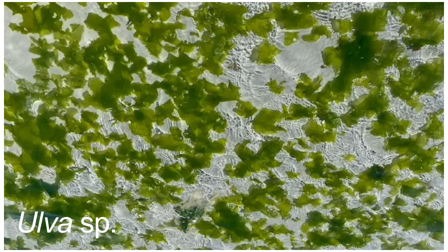
Sample Description	Scandium	Praseodymium	Neodymium	REE SUM	Copper	Nickel	Cobalt
Ulva cf. linza 2068	**3.52E+05**	**4.81E+05**	**4.79E+05**	**4.85E+05**	**1.08E+05**	**3.82E+04**	**7.54E+04**
Ulva sp. 2067	2.25E+05	3.43E+05	3.22E+05	3.39E+05	**1.35E+05**	**4.16E+04**	**5.68E+04**
Ulva sp. 2074	1.58E+05	1.80E+05	1.76E+05	1.97E+05	**7.52E+04**	**3.91E+04**	**4.31E+04**
Gracilaria sp. 2059	3.22E+04	8.46E+04	8.45E+04	7.91E+04	**5.33E+04**	**1.04E+04**	**1.43E+04**
Mazzaella sp. 2062	3.98E+04	4.98E+04	4.72E+04	5.27E+04	**6.36E+04**	**1.82E+04**	**1.17E+04**
Gracilaria sp. 2060	4.23E+04	1.38E+05	1.29E+05	1.31E+05	**5.75E+04**	**1.65E+04**	**1.32E+04**
Sargassum muticum 2075	1.37E+04	2.37E+04	2.40E+04	2.70E+04	**2.18E+04**	**1.31E+04**	**2.00E+04**
Fucus sp. 2076	1.81E+04	2.82E+04	2.96E+04	3.66E+04	**3.95E+04**	**4.89E+04**	**5.30E+04**
Unidentified diatom 21629	6.37E+04	6.58E+04	6.29E+04	8.81E+04	**3.95E+04**	**2.77E+04**	**1.66E+04**

Color code: *red values higher and blue colors lower values*


Sargassum muticum

https://www.uib.no/en/rg/mb/58943/will-rising-sea-temperatures-increase-impacts-invasive-seaweeds

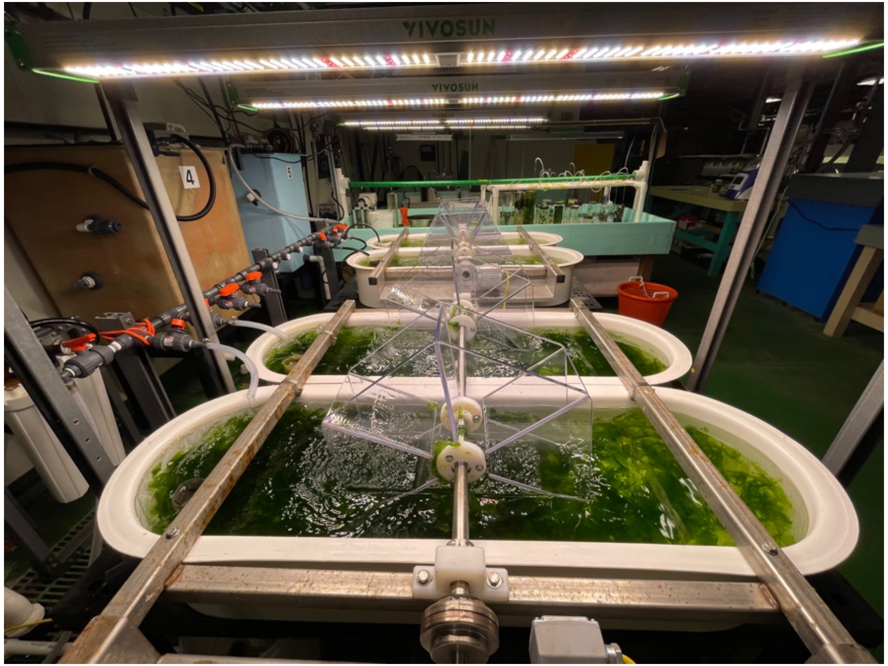

Gracilaria sp.

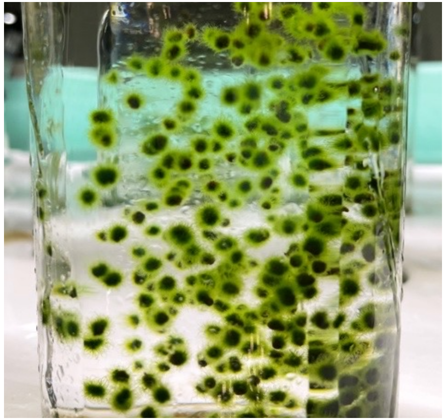

Ulva sp.

Marine Wet Lab Cultivation

Marine Algae Cultivation R&D

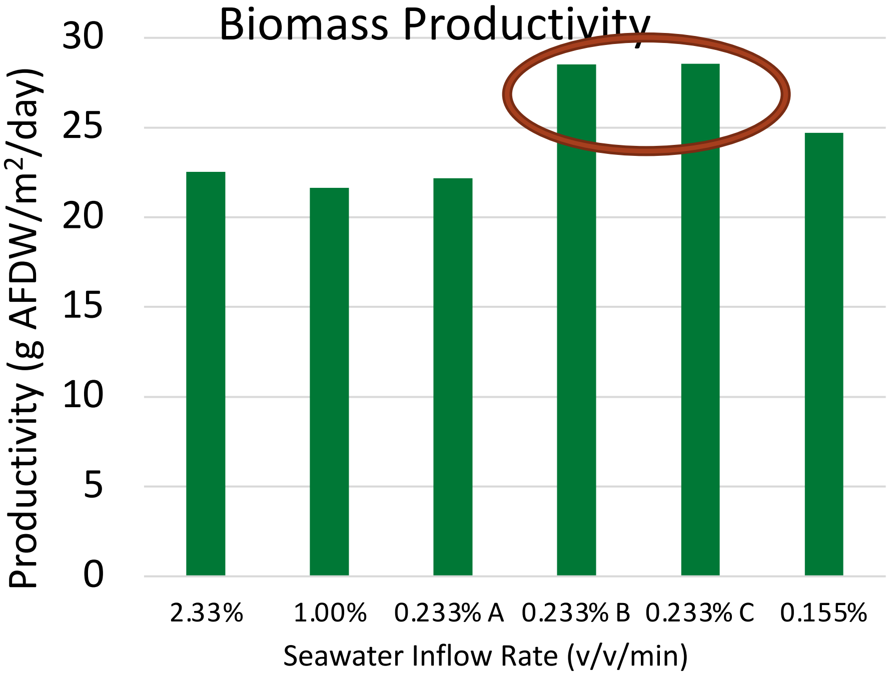
- Best management practices for maintaining living macroalgal cultivar stocks and seaweed mass production defined

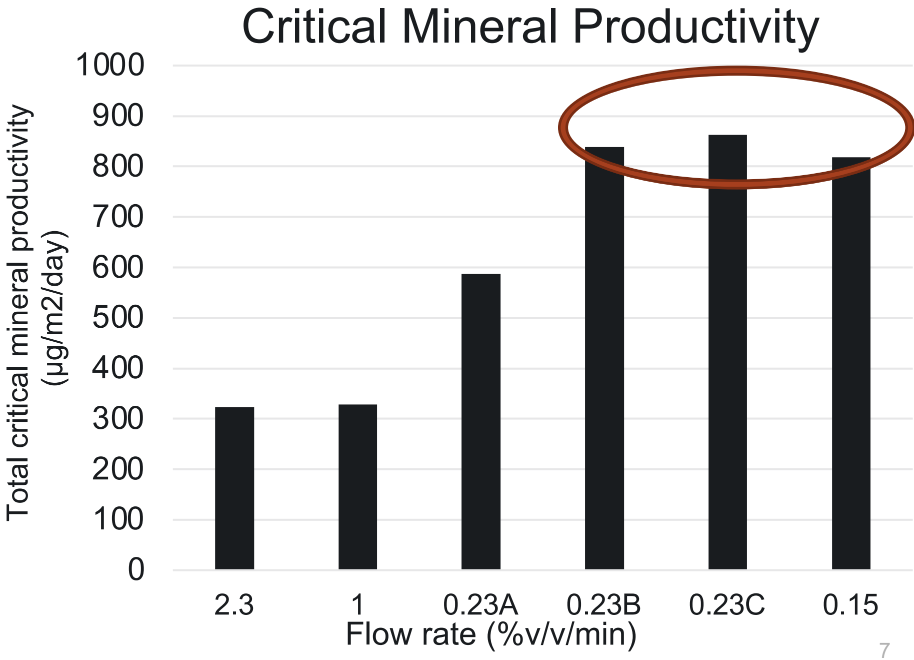




Marine Wet Lab Cultivation

Optimal flow rates for biomass and mineral productivity determined





Marine Wet Lab Cultivation

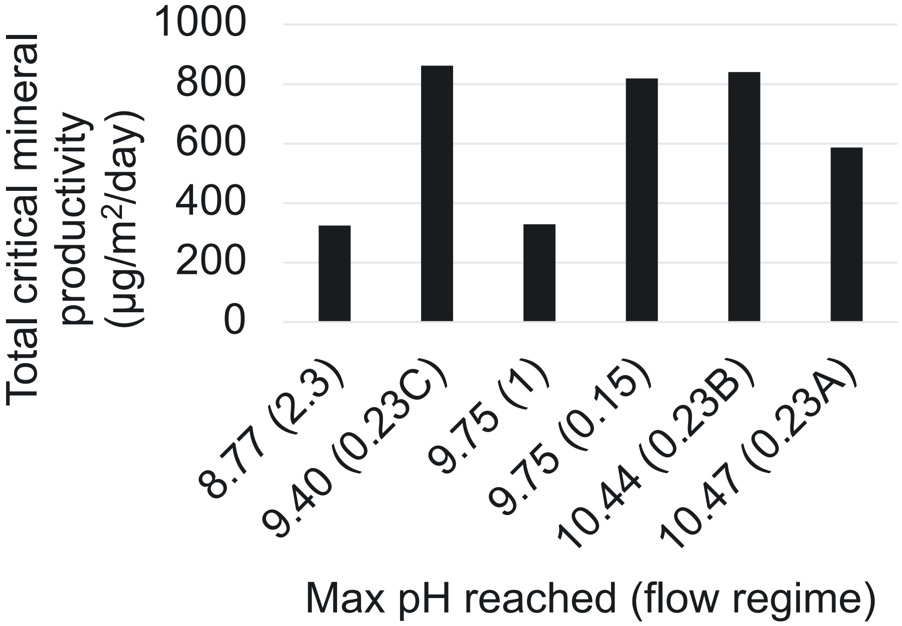
Exploring the practical effect of pH on mineral productivity

- pH is dependent on:
    - Seawater inflow rate
        - seawater alkalinity
        - dissolved carbon dioxide
    - Photosynthetic activity
        - Biomass density
        - Light intensity

- No clear trend of mineral productivity with maximum pH

- Generally, higher pH yielded greater critical mineral.

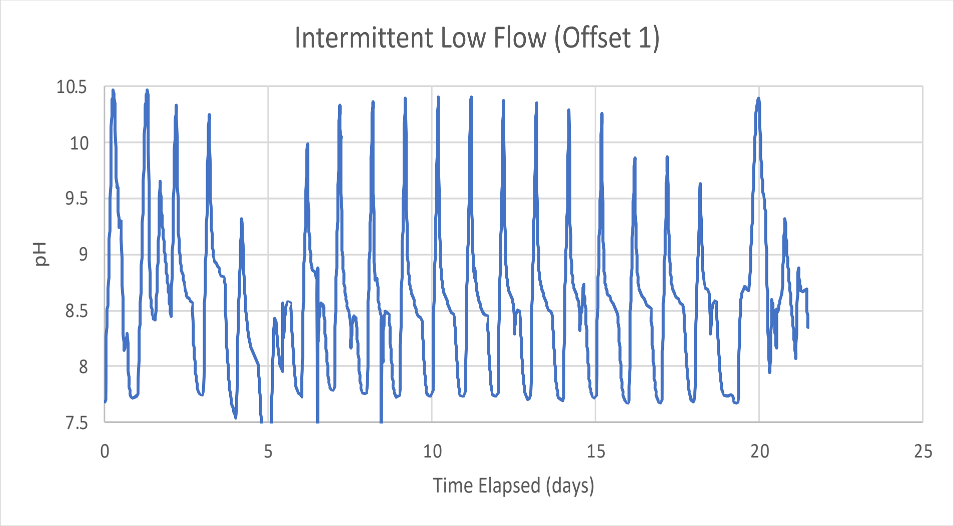
- Dynamics of pH and mineral content are likely element specific

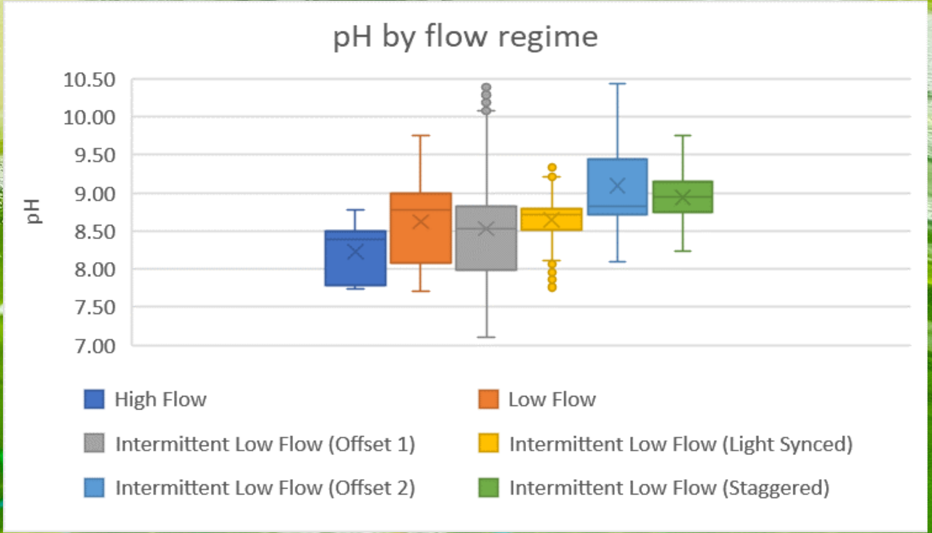


Marine Wet Lab Cultivation

Seawater pH dynamics during cultivation

Daily pH fluxes are highly variable





Hydrothermal Processing

Sequential processing to the macroalgae feedstock

Stage 1
<200 °C

- Polysaccharides for fermentation
- Solid residual to Stage 2

Stage 2
350 °C

- Biocrude oil for fuels
- Ash for nutrient recovery
- Nitrogen recovery from aqueous phase

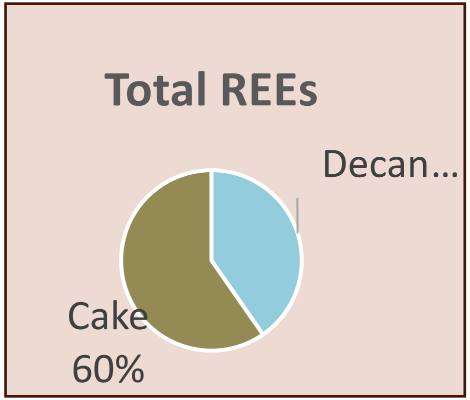
- Based on earlier work on kelp (Elliott et al. 2014), thermal pre-treatment improves dewatering and pumpability leading to higher yields
- Algae HTL research in FY 2021 and beyond will focus on applying sequential HTL to macroalgae and turf scrubbers
- Use process modeling to optimize fuel, starch, and nutrient outputs

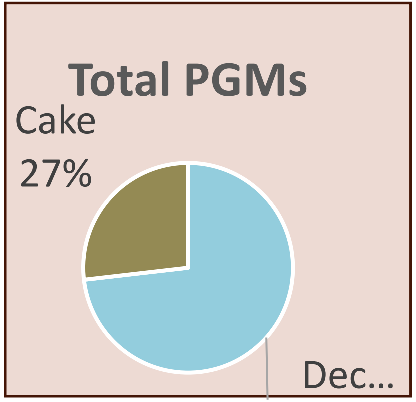
- **Make it pumpable**
- **Concentrate solids**
- **Generate REE-rich ash**

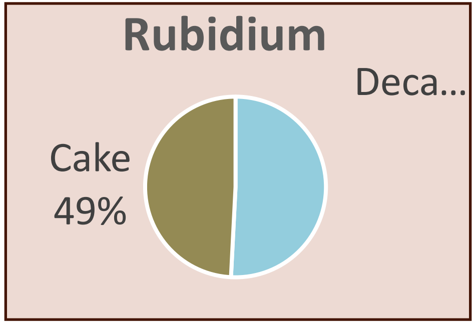
Elliott, D.C., Todd R. Hart, Gary G. Neuenschwander, Leslie J. Rotness, Guri Roesijadi, Alan H. Zacher, and Jon K. Magnuson. Hydrothermal Processing of Macroalgal Feedstocks in Continuous-Flow Reactors. *ACS Sustainable Chemistry & Engineering* **2014** *2* (2), 207-215 DOI: 10.1021/sc400251p

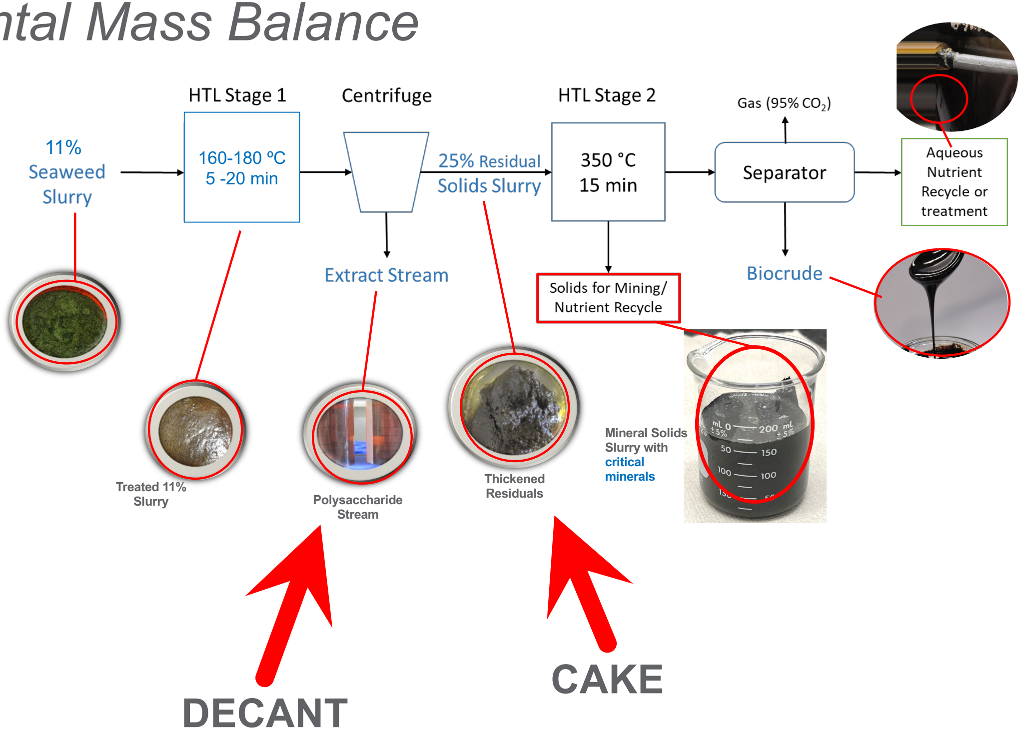
Hydrothermal Processing

Stage-1 Elemental Mass Balance





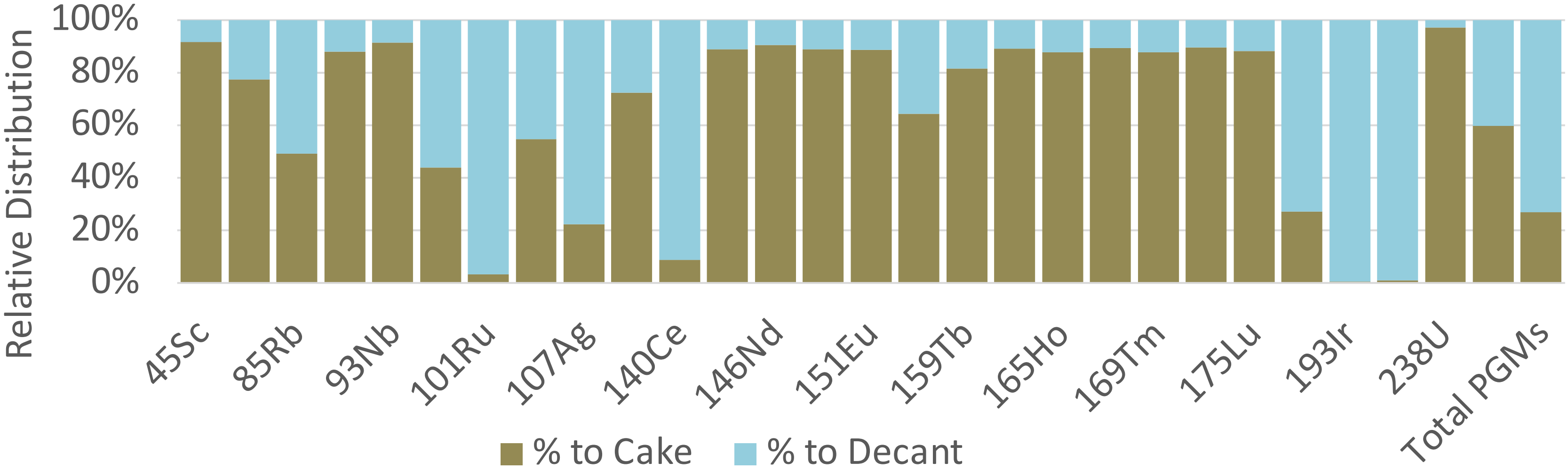




- The goal of any preprocessing step should be the *selective concentration* of elements of interest.
- Overall, not selective to the cake as hypothesized

Hydrothermal Processing

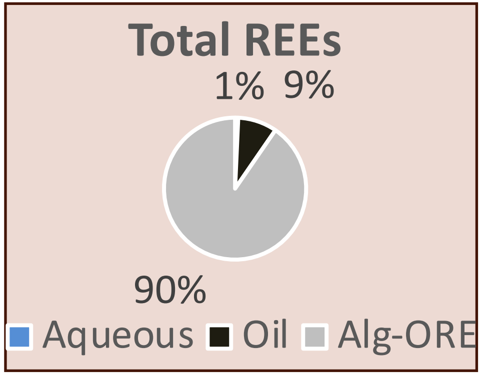
Stage-1 Elemental Mass Balance

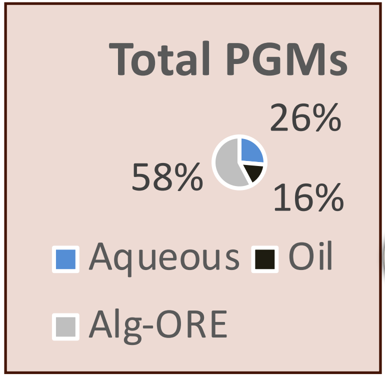


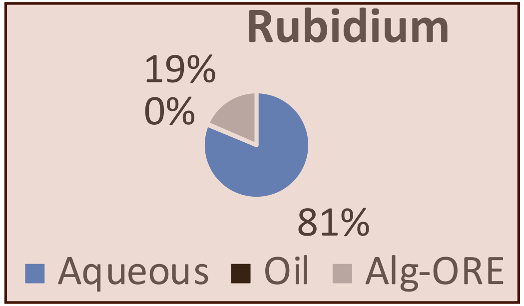
- The goal of any preprocessing step should be the *selective concentration* of elements of interest.
- Good selectivity for many REEs (e.g., Nd and Sc), notably NOT Ce

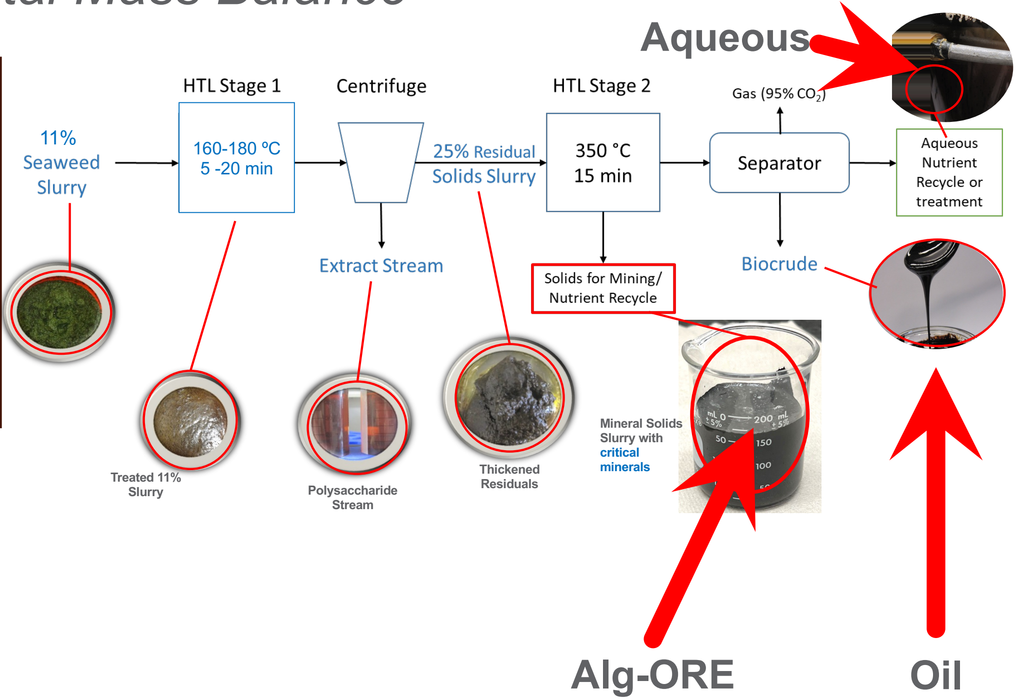
Hydrothermal Processing

Stage-2 Elemental Mass Balance








Aqueous

11% Seaweed Slurry

HTL Stage 1

160-180 °C
5 -20 min

Centrifuge

25% Residual Solids Slurry

HTL Stage 2

350 °C
15 min

Separator

Gas (95% CO_2)

Aqueous Nutrient Recycle or treatment

Extract Stream

Solids for Mining/ Nutrient Recycle

Biocrude

Treated 11% Slurry

Polysaccharide Stream

Thickened Residuals

Mineral Solids Slurry with **critical minerals**

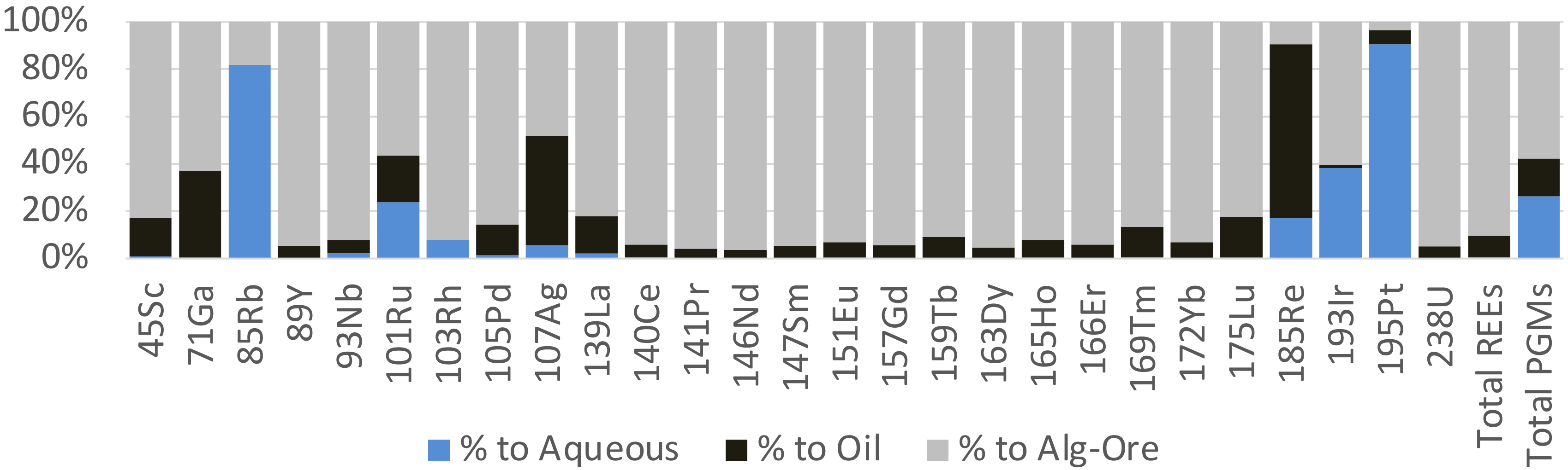
Alg-ORE

Oil

- Stage 2 results are more selectively separating critical minerals
- Overall, REEs and PGMs more selective to the Alg-ORE phase

Hydrothermal Processing

Stage-2 Elemental Mass Balance



- Very good selectivity for most REEs
- Oil phase has surprising amount of minerals (especially Re and Ag)
- Platinum in aqueous phase needs to be examined more closely

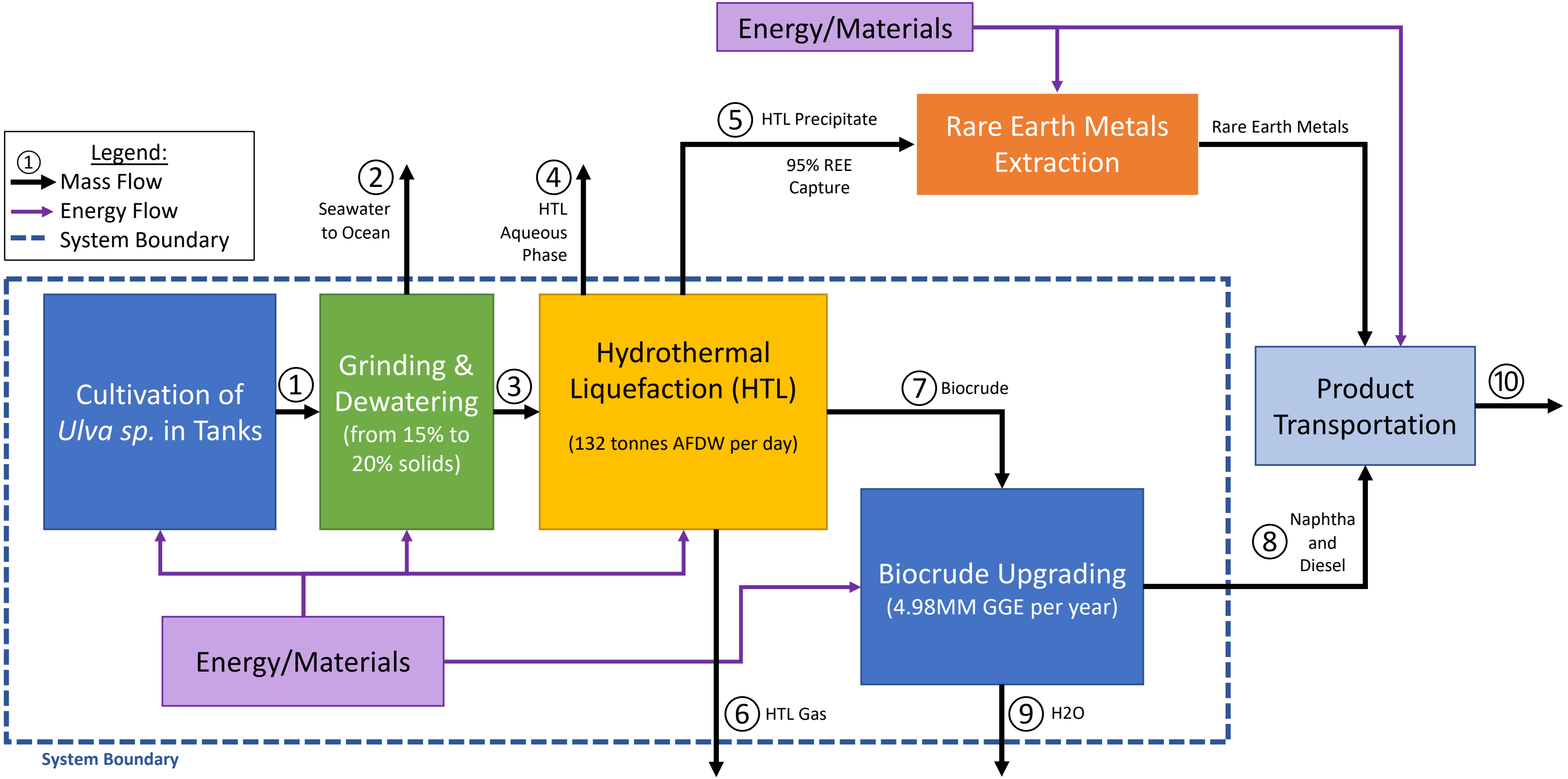
Techno-Economic and Life-Cycle Modeling

Facility Size and Outputs

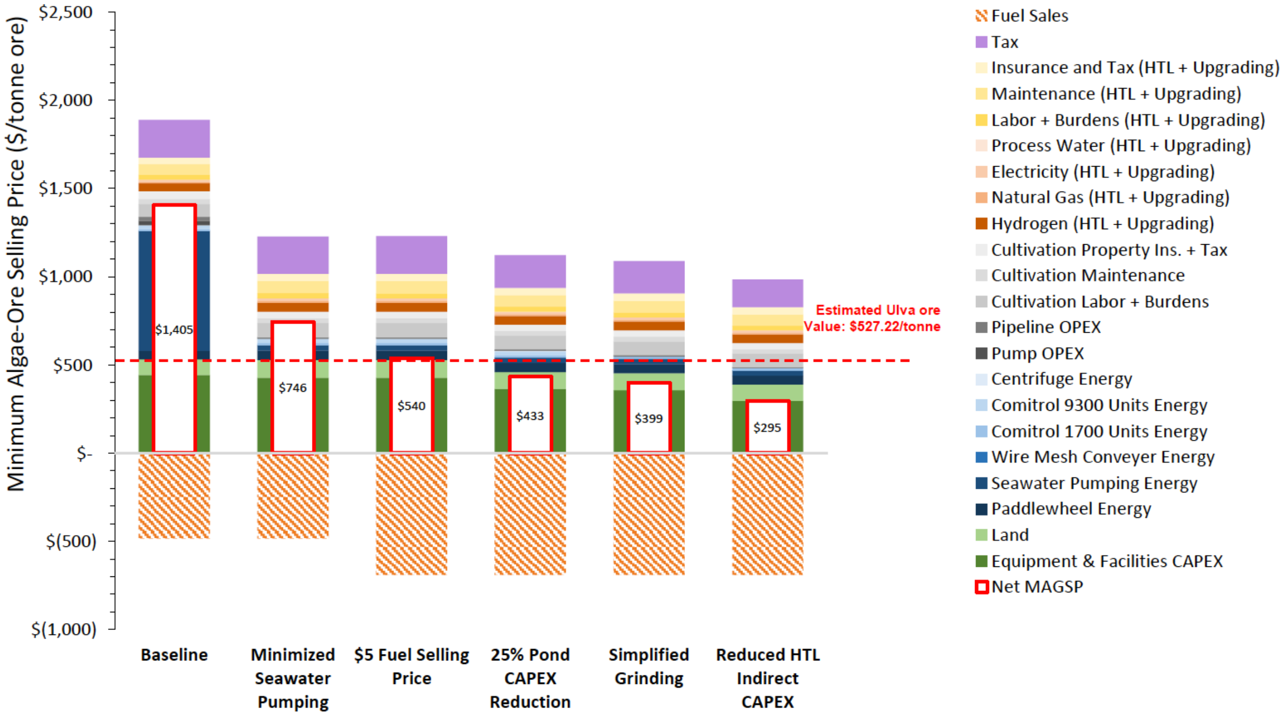
Parameter	Value	Units
Facility Size (acres)	1000	Wetted-acres
Facility Size (ha)	405	Wetted-hectares
Productivity	32.5	g AFDW m^{-2} day^{-1}
Biomass Output	43.4	Million Tonnes AFDW per year
Fuel Output	4.98	Million GGE per year
Algae-ore Output	29,014	Tonnes algae-ore per year
Scandium	*320*	*kg/yr*
Copper	*555*	*kg/yr*
Nickel	*720*	*kg/yr*
Rubidium	*556*	*kg/yr*
Rhenium	*172*	*kg/yr*

Techno-Economic and Life-Cycle Modeling

Process Flow Diagram and System Boundaries



Potential process improvements to lower the minimum algae-ore selling price (MAOSP).

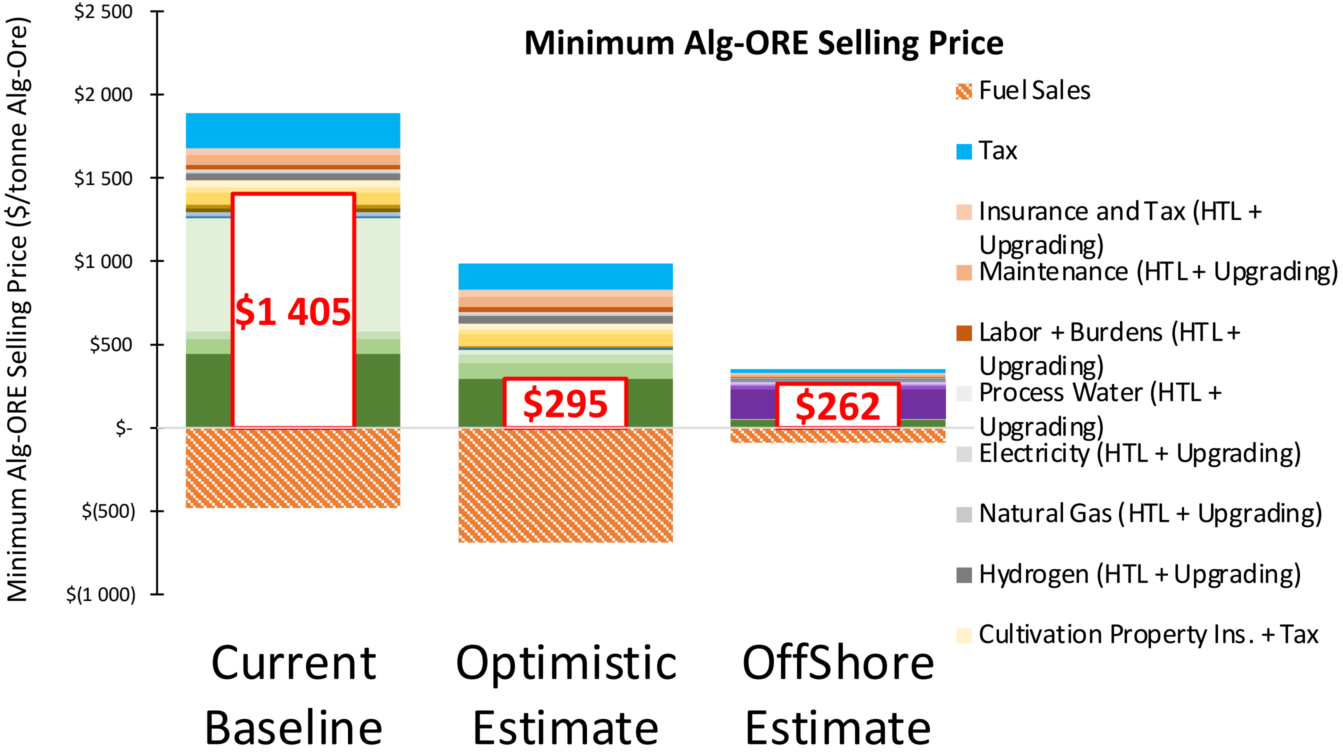


Process improvements compound from left to right and the scenarios with a total MAOSP below the dotted red line n scenarios where the cost of production is less than the total value of the ore

Techno-Economic and Life-Cycle Modeling

Open Ocean Cultivation of Seaweed Biomass

- Cost of production embodied in \$300 per dry tonne biomass purchasing cost – "Feedstock Production"
- Seaweed transportation costs included
  - \$36.66/DMT for loading/unloading to vessel
  - \$9.17/DMT for ocean transport
  - \$28.50/DMT for transport to processing facility
  - 350-acre processing facility
- Off-shore feedstock production and transportation costs shown in purple



Summary of Findings

- Reduced seawater flow rates correspond to higher levels of mineral productivity, without reducing biomass productivity.
- Exploring additional bioproducts outside of minerals and fuels, to complement a biorefinery approach
- **Stage-1** hydrothermal pretreatment did NOT improve the solids content or pumpability. Significant loss of REEs and PGMs to the aqueous phase decant.
- **Stage-2** hydrothermal liquefaction resulted in a concentration of primary critical minerals of interest (REEs and PGMs) to the Alg-ORE phase.
- Life Cycle Assessments show a clear pathway to low and even **negative** carbon fuels and mineral ores.


Extracted Ulvans

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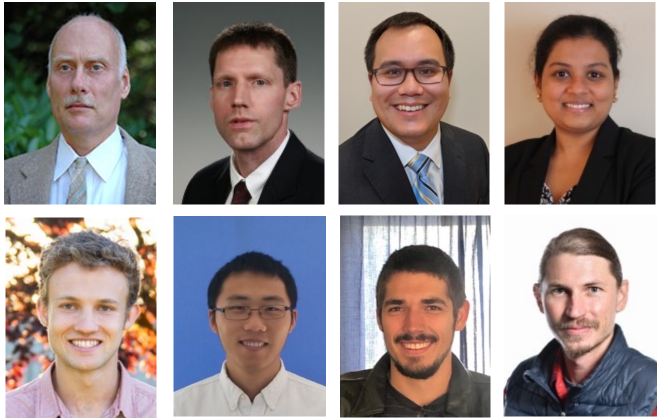

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Exploring Macroalgae as Critical Mineral Crops

E = (MC)^2

Exploring Macroalgae as Critical Mineral Crops

Next Steps

Macroalgal Crop Survey

Comparatively quantify the mineral content (REEs and PGMs) for candidate marine macroalgae with demonstrated cultivation capacity or natural abundance (e.g., *Sargassum*).

[REE] 10^{-12}

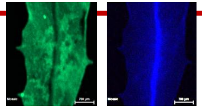
- Macroalga 1
- Macroalga 2
- Macroalga 3
- Macroalga 4

[REE] 10^{-6}

Down Selection

Characterization of REE and PGM in macroalgal tissues

Determine holding capacity. Define uptake rates in seawater matrix. Spatial visualizations via XRF.



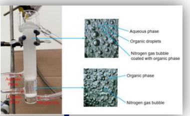
Nondestructive removal of REE/PGMs from macroalgal tissues

Define a functional biolixiviant and protocol for nondestructive recovery

[REE] 10^{-5}

Metal-Stripped Biomass

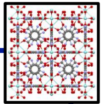
Lixiviant Recycle



Decomplexation

Regenerate the lixiviants (organic acids) through solvent extraction with complexing extractants

[REE] 10^{-4}



Metal-Organic Framework (MOF) selective adsorption and preconcentration

Use a high-salt compatible MOF to further concentrate REEs and PGMs

[REE] 10^{-3}

REE Refinement

Separate mixed REEs into individually separated, high-purity products

99% REE

PGM Refinement

Separate mixed PGMs into individually separated, high-purity products

99% PGM

Cascade Biorefinery

- REEs
- PGMs

- Biofuels
- Alginate
- Mannitol
- Protein
- Fertilizer

Economic viability determined through **techno-economic analysis**

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Questions?

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Final Project Report:

https://www.pnnl.gov/publications/unrealized-critical-lanthanide-extraction-sea-algae-mining-uncle-sam-domestic

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